MODERN DICTIONARY

INORGANIC CHEMISTRY

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An excellent up-to-date reference book for terminology of Inorganic Chemistry written in a simple and lucid language. The book covers the entire range of important Inorganic Chemistry terms for the use of undergraduates and general reader interested in this branch of the subject. Many related chemistry terms have also been included. This unique and concise book is indispensible for undergraduates and provides a systematic and authoritative material to the teacher.

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Dedicated
To
Prof M Satake
Fukui University, Japan
on his Birth Day

Preface

With more and more specialization and expansion of the subjects, it has become necessary to bring out the dictionaries in these special fields, particularly in modern sciences. Keeping this in view, the present volume has been written to provide students at undergraduate level, a concise view of Inorganic Chemistry in the form of a dictionary. The entries have been made in a clear and lucid manner to provide both straight forward definitions and essential details. Figures have been included, wherever necessary, to make the subject matter clear.

My colleagues Prof M Satake (Fukui University) and Prof T Nagahiro (Hemeji Institute of Technology) have helped me a lot in compiling the matter and bringing it in this form. I am grateful to them. I am also thankful to many of my friends in Delhi (India) who have helped me to bring out this publication from India.

I would most welcome the suggestions for its improvement.

G KANO

A

Acid rain. Man's impact on atmospheric chemistry is steadily increasing with progressive industrialization and urbanization. In the last few decades precipitation in serveral areas of the world has become increasingly more acidic. The term Acid rain is used to describe all precipitation rain, snow, sleet, etc. that has a pH less than 5.6, the pH expected in pure rain.

Acid rain is produced due to increase in sulphuric acid and nitric acid aerosols by fossil fuel combustion, metal smelting and industrial processes. Sulphur dioxide and nitrogen oxides are the two main culprits responsible for the acidic precipitation problem.

The study of precipitation chemistry is a relatively new field and the understanding of the phenomenon is limited. However, on the basis of available information, ecological effects of acid rain are far reaching, insidious often irrevesible and operating slowly in complex ways. In regious where acid neutralizing capacity of soils and water is low, the pH of streams and lakes have decreased and the metal concentration has increased. Aquatic organism have been affected at all tropic levels, abundance, production and growth have reduced and sensitive species have been lost. Other effects include changes in nutrient budgets of forest, agricultural lands, loss of soil fertility and decrease in the crop and forest productivity, corrosion and deterioration of materials. In the coming years due to the escalating rate of energy demand and industrialization, acid precipitation problems are likely to intensify.

Acid salt (acidic salt). It is a salt in which there is only partial replacement of the acidic hydrogen of an acid by metal or other cations. For polybasic acids the formulae are of the type $NaHSO_4$ (sodium hydrogensulphate) and $Na_3H(CO_3)_2.2H_2O$ (sodium sesquicarbonate). For monobasic acids such as

HF the acid salts are of the type KHF_2 (potassium hydrogen fluoride).

Acids and bases. The word acid comes from a Latin word *acidus* meaning sour, since a sour taste was one of the earliest recognised properties of this class of substances.

Arrhenius Definition As early as 1867 Arhenius defined an acid to be a substance which dissociates to yield hydrogon ion in aqueous solution. Similarly, an aqueous solution of a base gives hydroxyl ion in solution.

Thus,

$$\underset{\text{acid}}{HCl(aq)} \rightleftharpoons H^+(aq)+Cl^-$$

$$\underset{\text{base}}{NaOH(aq)} \rightleftharpoons Na^+(aq)+OH^-(aq)$$

This definition is of limited application and is valid only in aqueous solution. It does not cover other substances that do not contain H^+ and OH^- ions but can neutralize bases and acids respectively.

Bronsted-Lowry concept In 1923, a more general concept of acids and bases was introduced independently by J.N. Bronsted of Denmark and T.M. Lowry of England. According to Bronsted-Lowry definition, an acid is a substance that gives up a proton and a base is a substance that accepts a proton.

In a typical acid-base reaction,

$$HX+B \rightleftharpoons X^-+HB^+$$

HX being a proton donor is an acid and B being a proton acceptor is a base in the forward reactions. In the back reaction HB^+ being a proton donor is an acid and X^- being a proton acceptor is a base. To make a distinction between the two acids and two bases, those on the right-hand side of the equation are referred to as the conjugate acid and the conjugate base. Thus HB^+ is a conjugate acid of the base B and X^- is a conjugate base of acid HX. $HX—X^-$ and $HB^+—B$ constitute two conjugate acid-base pairs. The acid and base in each conjugate differ by a proton, In order that an acid may exhibit its acidic properties there must be a proton acceptor (base) present. Some examples are:

$$\begin{array}{lclclcl}
\textit{Acid} & & \textit{Base} & & \textit{Conjugate acid} & & \textit{Conjugate base} \\
HCl & + & H_2O & \rightleftharpoons & H_3O^+ & + & Cl^- \\
HSO_4^- & + & NH_3 & \rightleftharpoons & NH_4^+ & + & SO_4^{2-} \\
NH_4^+ & + & H_2O & \rightleftharpoons & H_3O^+ & + & NH_3
\end{array}$$

—conjugate—

conjugate

Thus, according to this concept neutralization is a process of transfer of a proton from an acid to a base. Some more examples may be cited as:

$$\begin{array}{lclclcl}
CH_3COOH & + & NH_3 & \rightleftharpoons & NH_4^+ & + & CH_3COO^- \\
NH_4^+ & + & S^{2-} & \rightleftharpoons & HS^- & + & NH_3 \\
[Fe(H_2O_6]^{3+} & + & H_2O & \rightleftharpoons & H_3O^+ & + & [Fe(H_2O)_5(OH)]^{2+}
\end{array}$$

Lux Flood concept The proton plays a vital role in explaining the acid-base behaviour in the Bronsted-Lowry concept. It was observed by Lux (1939) that the acid-base reactions are also feasible in oxide systems without the aid of protons. This approach was extended by Flood (1947) and applied to non-protonic systems which were not covered by the Bronsted-Lowry concept. According to the Lux-Flood definition, a base (like CaO, BaO or Na_2O) is an oxide ion donor and an acid (like SiO_2, CO_2 or P_4O_{10}) is an oxide ion acceptor. Some acid-base reactions, in terms of the Lux-Flood concept may be written as:

$$\begin{array}{lclcl}
\textit{Base} & & \textit{Acid} & & \\
CaO & + & SiO_2 & \rightarrow & CaSiO_3 \\
BaO & + & CO_2 & \rightarrow & BaCO_3 \\
6Na_2O & + & P_4O_{10} & \rightarrow & 4Na_3PO_4
\end{array}$$

The concept is particularly applicable to reactions which take place at high temperature, i.e. in metallurgical operations or during the manufacture of ceramics and glass. The approach can be extended to include other negative ion systems (like halides, sulphide or carbanions).

Cady Elsey concept The Arrhenius theory of acids and bases in aqueous solution was extended to liquid ammonia solvent system by Cady and Elsey. According to this theory, water ionizes as:

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

Similarly, liquid ammonia ionizes and produces ammonium ion, NH_4^+ and amide ion NH_2^-.

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

According to Cady-Elsey concept, any substance that can produce the cation characteristics of ammonia, i.e. NH_4^+ ion in liquid ammonia will behave as an acid in liquid ammonia. For example, NH_4NO_3 ionizes in liquid ammonia according to the equation.

$$NH_4NO_3 \rightleftharpoons NH_4^+ + NO_3^-$$

This ionization produces NH_4^+ ion which is a cation charactristics of ammonia. Therefore, NH_4NO_3 will have as an acid in liquid ammonia.

Similarly any substance that can produce the anion charactristic of ammonia, i.e. NH_2^- ion, in liquid ammonia will behave as a base in liquid ammonia. For example, $NaNH_2$ ionizes in liquid ammonia according to the equation.

$$NaNH_2 \rightleftharpoons Na^+ + NH_2^-$$

This ionization produces NH_2^- ion, which is an anion characteristic of ammonia. Therefore, $NaNH_2$ will behave as a base in liquid ammonia.

The process of neutralization is the combination of ammonium ion and the amide ion.

$$NH_4^+ + NH_2^- \rightleftharpoons 2NH_3$$

For example :

$$NH_4NO_3 + NaNH_2 \rightleftharpoons NaNO_3 + 2NH_3$$

Usanovich concept A very comprehensive definition of acids and bases was proposed by Russian chemist Usanovich (1939). According to him, "An acid is any chemical species which reacts with bases, gives up cations, or accepts anions or elections, or conversely, a base is any chemical species which reacts which acids, gives up anions or electrons, or combines with cations." The definition covers all Lewis acids and bases and includes redox reactions which may consist of complete transfer of one or more electrons. Some examples of acid-base reactions in terms of Usanovich concept are given below:

$$\underset{\textit{Acid}}{SO_3} + \underset{\textit{Base}}{Na_2O} \rightarrow Na_2SO_4$$

(acid SO_3 combines with anion O^{2-}; base Na_2O gives up anion O^{2-})

$$Sb_2S_5 + 3(NH_4)_2S \rightarrow 2(NH_4)_3SbS_4$$

(acid Sb_2S_5 combines with anion S^{2-}; base $(NH_4)_2S$ gives up anion S^{2-}).

$$Cl_2 + 2Na \rightarrow 2NaCl$$

(acid Cl gains an electron; base Na loses an electron).

$$Fe(CN)_2 + 4KCN \rightarrow K_4Fe(CN)_6$$

(acid $Fe(CN)_2$ combines with CN^- anions; base KCN gives up CN^-)

The unsaturation involved in certain acid-base reactions was also considered by Usanovich;

$$O{=}C{=}O + OH^- \rightarrow HOCOO^-$$

Thus we find that Unsanovich concept is like a synthesis of all the previous acid-base theories and in the process it has become too general. Having gone through several concepts of acid-base reactions, it becomes difficult to make an appropriate choice for the best. As a matter of fact, each concept has its plus and minus points. In his book, Moeller has very rightly concluded the discussion on acid-base concepts with the remarks, "Actually each concept is correct as far as it goes, and knowledge of the fundamentals of all is essential."

Acid solvents, Basic solvents. Solvents which have a strong tendency to give protons are also called acid solvents, e.g.

liquid hydrogen fluoride, H_2SO_4, CH_3COOH. Solvents which have a strong affinity for protons are called basic solvents, e.g. liquid ammonia, pyridine, hydrazine, etc.

Actinide contraction. The ionic radius decreases regularly as we move across the actinides. It is because of the poor shielding of the nuclear charge by the 5f electrons. The decrease being analogous to lanthanide contraction is called actinide contraction.

Actinides. The fourteen elements, following actinium, Ac (atomic number 89) from thorium (at. no. 90) to lawrentium (at. no. 103) are called the actinides. They result from the filling of the 5f orbitals and are analogous to the lanthanides. Actinium, like lanthanum, is also included in the actinide series.

Thorium, protactinium and uranium are naturally occuring while the rest are artificially prepared. Elements following uranium are termed transuranic elements.

Every known isotope of the actinides is radioactive and it is only because the half-lives of ${}^{232}_{90}Th$, ${}^{235}_{92}U$ and ${}^{238}_{92}U$ are of the same order of magnitude, as the age of the earth that they are still surviving.

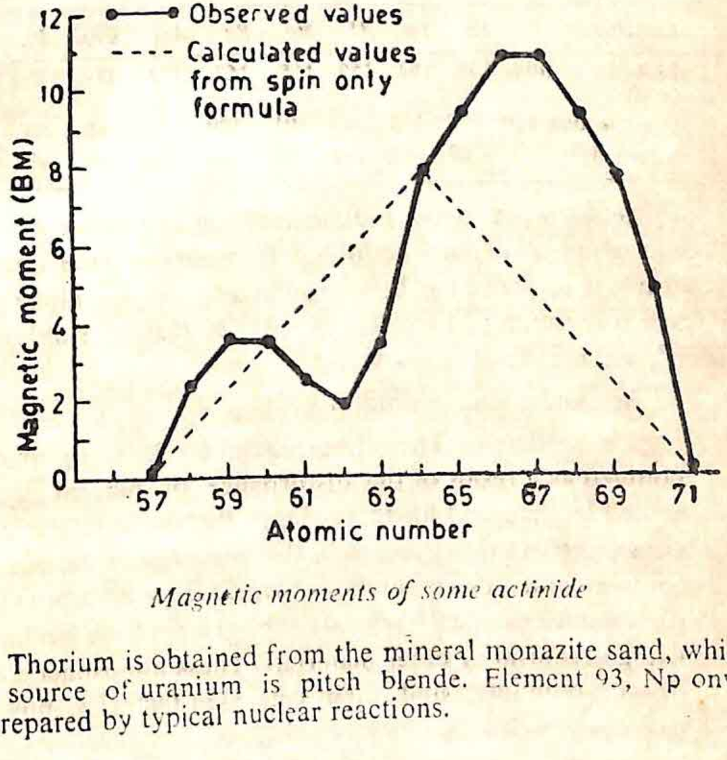
Thorium is widely distributed and its commercially important source is the monazite sand. Uranium is also widely distributed; its most important source is pitch blende, U_3O_8. The transuramic elements have been prepared artificially.

The elements are silvery white metals of high density with relatively high melting and boiling points. The metallic radii decrease sharply from Ac to U (table below) probably due to an increasing number of electrons being involved in metallic bonding. Thereafter (except Np and Pu) increasing metallic radius is presumably a result of fewer electrons being involved in metallic bonding.

On the other hand, the ionic radii in a given oxidation state fall steadily and indicate that some sort of "actinide contraction" exists.

The metals are reactive and tarnish rapidly in air. They react with most non-metals especially if heated. The elements do not react with alkalis and are less reactive towards acids. Th, U and Pu are rendered passive by conc. HNO_3. The presence of F^- ions prevents this and is the best method for dissolving the metals.

The magnetic moments of some ions of the actinides are shown in the following figure. The variations are compareble with the tripositive ions of the lanthanides.



Magnetic moments of some actinide

Thorium is obtained from the mineral monazite sand, while the main source of uranium is pitch blende. Element 93, Np onwards are prepared by typical nuclear reactions.

For the first three elements, Th, Pa and U, the most stable oxidation state is that involving all the valence electrons. It decreases progressively until in the second half of the series, +3 state becomes dominant. The various oxidation states are listed below:

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
						+2			(+2)	(+2)	(+2)	(+2)	**+2**	
+3	(+3)	(+3)	+3	+3	+3	**+3**	**+3**	**+3**	**+3**	**+3**	**+3**	**+3**	**+3**	**+3**
	+4	+4	+4	+4	**+4**	(+4)	(+4)	+4						
		+5	+5	**+5**	+5	+5								
			+6	+6	+6	+6								
				+7	+7									

A bold type indicates the most stable oxidation state whereas the unstable states are included in parentheses.

Metallic and ionic radii of actinides

Element	*Th*	*Pa*	*U*	*Np*	*Pu*	*Am*	*Cm*	*Bk*	*Cf*	*Es*
Metallic radius (pm)	179	163	156	155	169	173	174	170	185	186
Ionic radius M^{3+} (pm)	108	105	103	101	100	99	98	96	96	—
M^{4+}	99	96	93	92	90	89	88	83	82	—

Actinium. A toxic radioactive metallic element that is the first member of the actinides. It occurs in trace quantities in uranium ores and has been used as a source of alpha particles. Symbol: Ac; m.p. 1323 K; b.p. 3473 K (calc.); stablest isotope ^{227}Ac (half-life 21.6 years).

Actinoids. (See actinides).

Air pollution. The atmospheric air is being increasingly polluted as a result of the disturbance of natural equilibrium caused by man and his technology. By the term 'air pollution' we understand the presence in the atmosphere of one or more contaminants or combinations thereof, in such amounts and of such durations that they are or may tend to be harmful to living organism or other materials. These atmospheric contaminants (pollutants) find their origin in factories, power plants and motor vehicles.

Alkali metals (Group IA elements). The IA group of the periodic table consists of lithium (Li) sodium (Na), potassium (K) rubidium (Rb), cesium (Cs) and francium (Fr). These elements are highly reactive metals, which form strongly alkaline oxides and hydroxides. So they are commonly called as the alkali metals. The main characteristics of the elements are listed below.

Physical Characteristics of Alkali Metals

Property	Li	Na	K	Rb	Cs
Atomic number	3	11	19	37	55
Atomic mass	6.94	23	39.10	85.48	133
Atomic radius (Å)	1.23	1.57	2.03	2.16	2.35
Ionic radius (Å)	0.60	0.95	1.33	1.48	1.69
Atomic volume	12.97	23.68	45.86	55.80	69.95
Density (g cm^{-3})	0.534	0.972	0.860	1.530	1.903
Ionization energy (kJ mol^{-1})	520	496	419	403	375
Electronegativity	1.0	0.9	0.8	0.8	0.7
Melting point (K)	454	371	336	312	302
Boiling point (K)	1,609	1,153	1,035	973	943
Heat of atomization (kJ mol^{-1})	163.6	104.2	83.3	79.5	75.7
Specific heat at 273 K	0.941	0.293	0.17	0.08	0.049
Flame coloration	Crimson	Yellow	Lilac	Violet	Violet
$E°(V)(M^{+}+e^{-}-M)$	—3.04	—2.71	−2.92	—2.94	—2.99

The electronic configurations of the alkali metals are given below:

Element	*At. no.*	*Electronic configuration*	
Lithium	3	$2s^2, 2s^1$	or [He] $2s^1$
Sodium	11	$1s^2, 2s^2p^6, 3s^1$	or [Ne] $3s^1$
Potassium	19	$1s^2, 2s^2p^6, 3s^2p^6, 4s^1$	or [Ar] $4s^1$
Rubidium	37	$1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6, 5s^1$	or [Kr] $5s^1$
Cesium	55	$1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6, d^{10}, 5s^2p^6, 6s^1$	or [Xe] $6s^1$
Francium	87	$1s^2. 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^{10}, 6s^2p^6, 7s^1$	or [Rn] $7s^1$

Thus all of them possess one electron in their outermost orbit and they exhibit monovalency.

Alkali metals in ammonia. The ability to dissolve the alkali metals is one of the striking features of liquid ammonia as a solvent. The alkali metal solutions in ammonia are blue in colour. The blue solution is characterized by:

Its colour which is independent of the metal involved,

Its density which is similar to that of pure ammonia,

Its conductivity which is in the range of electrolytes dissolved in ammonia, and

Its paramagnetism (i.e. these solutions when placed in a magnetic filed are attracted into the field) which indicates the presence of a large number of unpaired electrons.

The alkali metal solutions dissociate to form alkali metal cations and solvated electrons.

$$\underset{\text{dissolved in liq. } NH_3}{M} \longrightarrow M^+ + [e(NH_3)_x]^-$$

The dissociation into cation and anion accounts for the electrolytic conductivity of the blue coloured dilute solutions. As the concentration of the solution is increased, M^+ and e^- species associate resulting in a decrease of conductivity.

Very dilute solutions of alkali metals in liquid ammonia are meta-stable and when catalysed they undergo decomposition.

$$[e(NH_3)_x]^- \xrightarrow{Fe_2O_3} NH_2^- + \tfrac{1}{2}H_2 + (x-1)NH_3$$

As the concentration of metal increases, the blue colour changes to bronze and finally the blue colour disappears altogether. On evaporating the alkali metal ammonia solutions, alkali metal can be recovered.

The blue colour of dilute metal ammonia solutions may be attributed to the presence of ammoniated cation and ammoniated electron.

$$M^+ + xNH_3 \rightleftharpoons \underset{\substack{\text{ammoniated} \\ \text{cation}}}{[M(NH_3)_x]^+}$$

$$e^- + yNH_3 \rightleftharpoons \underset{\substack{\text{ammoniated} \\ \text{electron}}}{[e(NH_3)_x]^-}$$

Alkaline earth metals. (Group IIA elements). The IIA group of the periodic table consists of beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba) and radium (Ra). Since these elements were alkaline and existed in the earth, they were called as alkaline earths, later on they were named as alkaline earth metals. All these metals consist of two electrons in their outermost s-orbital and closely resemble in physical and chemical properties. The main characteristics of the elements are listed below:

Physical Charecteristics of Group IIA Elements

Property	*Be*	*Mg*	*Ca*	*Sr*	*Ba*	*Ra*
Atomic number	4	12	20	38	56	88
Atomic mass	0.01	24.31	40.08	87.67	137.67	226.05
Atomic radius (A)	1.13	1.60	1.97	2.15	2.21	—
Ionic radius (A)	0.34	0.74	1.04	1.20	1.38	1.32
Atomic volume	4.90	13.97	25.91	34.54	36.72	38.00
Density (g cm^{-3})	1.85	1.74	1.54	2.6	3.5	6.00
Electronegativity	1.5	1.2	1.0	1.0	0.9	—
Melting point (K)	1553	924	1124	1073	1130	973
Boiling point (K)	2773	1383	1442	1423	1410	1413
Ionization energy (kJ mol^{-1})						
Ist	899	737	590	550	503	510.5
2nd	1757	1450	1145	1064	965	972.8
E^0 (V) (M^{2+}/M)	−1.70	−2.37	−2.87	−2.89	−2.90	—
Heat of atomization (kJ mol^{-1})	327.2	147.3	177.8	163.6	176.6	—
Heat of hydration of ions (kJ mol^{-1})	2,406	1,929	1,632	1,485	1,276	—
Specific heat	0.452	0.246	0.168	—	0.368	—
Flame coloration	—	—	Brick red	Crimson	Apple green	Crimson

The electronic configurations of alkali metals are given below:

Element	*At. no.*	*Electronic configuration*
Beryllium	4	$1s^2, 2s^2$ or [He] $2s^2$
Magnesium	12	$1s^2, 2s^2p^6, 3s^2$ or [Ne] $3s^2$
Calcium	20	$1s^2. 2s^2p^6, 3s^2p^6, 4s^2$ or [Ar] $4s^2$
Strontium	38	$1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6, 5s^2$ or [Kr] $5s^2$
Barium	56	$1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}, 5s^2p^66s^2$ or [Xe] $6s^2$
Radium	88	$1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}f^{14}, 5s^2p^6d^{10}$- $6s^2p^67s^2$ or [Rn] $7s^2$

Thus all of them possess two electrons in their outermost orbit and exhibit divalency.

Allotropes of antimony. Antimony exists in the following allotropic forms:

Yellow or α-antimony It is obtained by passing air through liquid stibine at 183 K.

$$4SbH_3+3O_2 \longrightarrow 4Sb+6H_2O$$

It is yellow non-metallic form of antimony. It is soluble in carbon disulphide. It is stable at low temperature and at room temperature it readily changes into black or β-antimony.

Black or β-antimony It is obtained as a black powder when yellow or α-antimony is allowed to stand at room temperature. It gradually changes into metallic form and rapidly on heating.

Explosive antimony It is obtained as steel grey powder by the electrolysis of antimony trichloride in hydrochloric acid using Pt cathode and Sb anode. On being heated or scratched it explodes and changes to metallic antimony followed by liberation of excessive heat. It is believed that explosive antimony is a solid solution of antimony chloride in yellow antimony.

Metallic antimony It is obtained as rhombohedral crystals by gradually cooling the fused antimony. It is grey coloured lustrous, very brittle and poor conductor of heat and electricity (m.p. 903 K, b.p. 1653 K, sp. gr. 6.58). Its structure is similar to that of metallic arsenic (Sb—Sb distance=0.5 Å).

Allotropes of arsenic. Arsenic exhibits three allotropic forms, viz. metallic or grey, yellow and black arsenic.

Metallic or grey arsenic It is the normal allotrope of arsenic grey in colour with dull metallic lustre, with sp. gr. 5.73. It sublimes at 886 K, giving yellow vapours. It is a good conductor of electricity. Its vapour density varies with temperature indicating the equilibrium $As_4 \rightleftharpoons As_2$. It is 98% As_4 at 1025 K and 98% As_2 at 1915 K. It nas layer-like structure with each atom having three equidistant pyramid-bonded atoms and three more neighbours of adjacent layer.

Yellow arsenic It is obtained by suddenly cooling of the arsenic vapours in a bath of liquid air in dark. It is unstable form with respect to other forms. It is solid like wax with sp. gr. 3.1. It is soluble in carbon disulphide and poor conductor of electricity. Like white phosphorus, it produces luminescence due to oxidation. It is non-metal (As—As=2.44 Å) just like white phosphorus.

Black arsenic This form of arsenic may be considered as an intermediate form of the above two mentioned forms. It may be obtained by dissolving yellow arsenic in carbon disulphide and allowing to stand for some time. It is black amorphous solid, poor conductor of electricity and less stable. Its sp. gr. is 4.6. It does not oxidize in air or nitric acid upto 355-365 K. It changes into metallic form by heating to 635 K in a tube.

Allotropes of white arsenic. There are three allotropes of white arsenic:

Amorphous form It is obtained by the condensation of arsenious oxide vapours very slowly below 475 K. It is a colourless amorphous form with glassy appearance. It is slightly soluble in water, and sublimes at 475 K. Its sp. gr. is 3.74. In air it gradually changes into octahedral crystalline form.

Crystaliine octahedral form. It is obtained by the rapid condensation of arsenious oxide vapours or on standing amorphous form in air for long time (m.p. 548 K, sp. gr. 3.69). It is the most stable form.

Crystalline monoclinic form It is obtained by prolonged heating of the above forms at 475 K or by the crystallization of aqueous solution of arsenious oxide in the presence of potassium hydroxide (m.p. 588 K, sp. gr. 3.85).

Allotropy. The existence of more than one form of an (uncombined) element is known as allotropy. Oxygen exhibits several allotropic forms (or allotropes); the most common are ordinary oxyen, O_2 and ozone, O_3.

Alloy. It is a mixture of two or more metals (e.g. bronze or brass) or of a metal with small amounts of non-metals, (e.g. steel). Alloys may be completely homogeneous mixtures or may contain small particles of one phase in the other phase.

Alnico. Any of a group of very hard brittle alloys used to make powerful permanent magnets. They contain nickel, aluminium, cobalt, and copper in different amounts. Iron, titanium, and niobium may also be present. They have a high remanence and coercive force.

Alpha particle. A particle which is commonly ejected from a nucleus lying beyond the trough of stability is the alpha particle. It is a complex particle composed of two protons and two neutrons and is identical to a helium nucleus.

Alumina. Hydrated alumina is the natural bauxite mineral, $Al_2O_3.nH_2O$ (n=1-3). Pure Al_2O_3 can be prepared in the laboratory by heating aluminium hydroxide or ammonium alum.

Freshly prepared alumina reacts with both acids and alkalis showing its amphoteric nature.

$$Al_2O_3+6H^+ \longrightarrow 2Al^{3+}+3H_2O$$
$$Al_2O_3+2OH^-+2H_2O \longrightarrow 2[Al(OH)_4]^-$$

Alumina is a refractory material used in the manufacture of heat resistant bricks and for the internal lining of furnaces. As a finely divided powder, it is often used as the adsorbing stationary phase in column chromatography. Alumina can be fused with oxides of chromium, iron and cobalt to form synthetic semi-precious stones. It is also used as a dehydrating agent, e.g.

$$\underset{\text{ethanol}}{CH_3-CH_2-OH} \xrightarrow[575\ K]{Al_2O_3} \underset{\text{ethylene}}{H_2C=CH_2} + H_2O$$

Aluminium. [Latin *alumen*, *aluminis*, alum]. A Group IIIA element of the third period of the Periodic Table of elements, atomic number 13, atomic mass 26.9815, one stable isotope, ^{27}Al (100 per cent). Aluminium metal was obtained by Wohler in 1827. Third to oxygen and silicon in abundance in earth's crust (8.8 per cent); various aluminosilicates containing these three elements make up 82 per cent of crust's mass. Does not occur in the free form: the most important source of aluminium is bauxtie.

Properties A silvery white metal, light, firm, ductile, a good conductor of heat and electricity. A highly reactive element, valence +3. Combines with oxygen and is covered by an oxide film. Al_2O_3 when stored in the air. This explains high corrosion resistance of aluminium. Remains unattacked under the action of conc. HNO_3· Readily dissolves in alkalis, dilute HCl and H_2SO_4. Like Al_2O_3 aluminium hydroxide is amphoteric: in aqueos solutions, it reacts with acids to give a hydrated ion, $[Al(H_2O)_6]^{3+}$, and with alkalis to give metal aluminates.

Extraction By the electrolysis of aluminium oxide made from bauxite and dissolved in molten cryolite, Na_3AlF_6.

Uses The production of light alloys (Dural, Silumin) for aircraft, automobiles; employed as building material, as material for chemical equipment, in the manufacture of electric wire, capacitors, in building of nuclear reactors. Aluminium is employed as reducing agent in metallurgy. Various aluminium compounds have practical applications.

Aluminium oxide, aluminium chloride, $AlCl_3$, and hydrated aluminium chloride, $AlCl_3.6H_2O$, are used as catalysts in the organic synthesis, aluminium sulphate, $Al_2(SO_4)_3.18H_2O$, and and potassium alum, $KAl(SO_4)_2.12H_2O$, as mordants in dyeing, for tanning leather, in th manufacture of paper, and in the purification of water. Silver paint used in building and architecture for protecting from corrosion and for decorative purposes in a mixture of aluminium powder and mineral oil. Organoaluminium compounds are employed as starting material for the synthesis of other organometallics; alkylaluminium derivatives are catalysts for the polymerization of olefines.

Aluminium chloride. Anhydrous aluminium chloride, Al_2Cl_6 is prepared by passing dry chlorine or HCl gas over heated aluminium powder

$$2Al+3Cl_2 \longrightarrow Al_2Cl_6$$
$$2Al+6HCl \longrightarrow Al_2Cl_6+3H_2$$

The other halides, viz. aluminium bromide and aluminium iodide can also be prepared by the action of corresponding halogen on the metal.

From the molecular mass determinations in organic solvents and in the vapour state (upto 658 K), it is inferred that the compound exists in the dimeric from. At high temperature (1000 K) it dissociates into monomer.

$$Ai_2Cl_6 \rightleftharpoons 2AlCl_3$$

Anhydrous Al_2Cl_6 reacts with water to give hydrated aluminium chloride, $AlCl_3.6H_2O$.

$$Al_2Cl_6+12H_2O \longrightarrow 2AlCl_3.6H_2O$$

The use of anhydrous aluminium chloride as a catalyst in Friedel-Crafts reaction is well known. It is also used in petroleum cracking and in the manufacture of dyes, drugs and perfumes.

Aluminium hydride (Alane). AlH_3 It is prepared by the reaction of lithium hydride with aluminium chloride in dry ether.

$$3LiH+AlCl_3 \longrightarrow 3LiCl+AlH_3$$

Aluminium hydride is obtained as a white solid. It is stable upto 373 K. above this temperature it decomposes into its components. It reacts with lithium hydride in ether to form a powerful reducing agent, lithium aluminium hydride.

$$LiH + AlH_3 \longrightarrow LiAlH_4$$

It is an electron deficient compound and acts as Lewis acid, e.g. $AlH_3.NH_3$, $AlH_3.N(CH_3)_3$, etc.

It hydrolyses violently to form aluminium hydroxide.

$$AlH_3 + 3H_2O \longrightarrow Al(OH)_3 + 3H_2$$

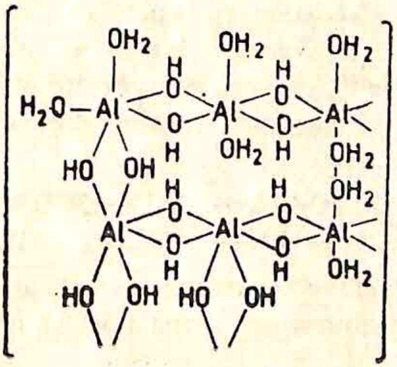
It is an insoluble polymer $(AlH_3)_n$. The structure is a giant molecule of AlH_2Al bridges confirmed by X-ray and neutron diffraction studies.

Aluminium hydroxide, Al(OH)$_3$. It is prepared as a colourless geletinous precipitate by the action of hydroxide solution with aluminium salt solution.

$$AlCl_3 + 3NH_4OH \longrightarrow Al(OH)_3 + 3NH_4Cl$$

The precipiate of aluminium hydroxide is amorphous and dries to a glassy solid.

It is amphoteric in its behaviour.



$$Al(OH)_3+3HCl \longrightarrow AlCl_3+H_2O$$
$$Al(OH)_3+3NaOH \longrightarrow 3Na_3AlO_3+3H_2O$$
$$Al(OH)_3+NaOH \longrightarrow NaAlO_2+2H_2O$$

It dissolves in sodium hydroxide to form hydroxy aluminate ions, e.g.

$$Al(OH)_3+OH^- \longrightarrow [Al(OH)_4]^-$$
$$Al(OH)_3+3OH^- \longrightarrow [Al(OH)_6]^{3-}$$

It is a polynuclear complex. It has a layer structure, such that each aluminium atom is associated with six OH groups and each OH group is associated with two aluminium atoms.

Aluminium oxide (Alumina), Al_2O_3. It is prepared by the thermal decomposition of aluminium salts.

$$Al_2(SO_4)_3 \longrightarrow Al_2O_3+3SO_2$$
$$4Al(NO_3)_3 \longrightarrow 2Al_2O_3+12NO_2+3O_2$$
$$2Al(OH)_3 \longrightarrow Al_2O_3+H_2O$$

The precipitate of aluminium hydroxide is obtained by the action of aluminium salts and ammonium hydroxide.

$$AlCl_3+3NH_4OH \longrightarrow Al(OH)_3+3NH_4Cl$$

Alumina is white amorphous powder (m.p. 2325 K, b.p. 3255 K) and amphoteric in nature.

$$Al_2O_3+3H_2SO_4 \longrightarrow Al_2(SO_4)_3+3H_2O$$
$$Al_2O_3+2KOH \longrightarrow 2KAlO_2+H_2O$$

Alumina is a very stable compound. It does not reduce to the metal. It is only reduced with great difficulty.

Its mixture with carbon, when heated at high temperature in the presence of nitrogen, gives aluminium nitride which is hydrolysed by water.

$$Al_2O_3+3C+N_2 \longrightarrow 2AlN+3CO$$
$$AlN+3H_2O \longrightarrow Al(OH)_3+NH_3$$

It reacts with carbon or calcium carbide at very high temperature to form aluminium carbide which on hydrolysis gives methane.

$$2Al_2O_3+9C \longrightarrow Al_2C_3+6CO$$
$$2Al_2O_3+3CaC_2 \longrightarrow Al_4C_3+3CaO+2CO$$
$$Al_4C_3+12H_2O \longrightarrow 4Al(OH)_3+CH_4$$

It is used for the manufacture of aluminium and its salts. It is used as a refractory material, medium in chromatographic separation. Fused alumina at 3275 K (in an arc furnace) is known as alundum or artificial carundum, it is used as an abrassive. Fused mixture of alumina and lime is known as bauxite cement which is resistent to sea water and sets quickjy.

Aluminium potassium sulphate (potash alum, $K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$). It is also known as common alum. It is prepared by concentration of calculated quantities of potassium sulphate and aluminium sulphate solutions. On cooling crystals of potash alum separate out.

$$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \longrightarrow K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$$

It is manufactured from alum stone, $K_2SO_4 . Al_2(SO_4)_3 . 4Al(OH)_3$ by dissolving it in sulphuric acid when aluminium hydroxide changes into aluminium sulphate. A calculated quantity of potassium sulphate is added to it and on crystallization, alum separates out.

Alum shale ($Al_2O_3 . xSiO_2 + FeS_2$) is also used for the manufacture of potash alum. It is first roasted in the excess of air when iron sulphide changes into ferrous sulphate and sulphuric acid. The latter converts the alumina into aluminium sulphate.

$$2FeS_2 + 2H_2O + 7O_2 \longrightarrow 2FeSO_4 + 2H_2SO_4$$
$$Al_2O_3 . xSiO_2 + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + xSiO_2 + 3H_2O$$

Ferrous sulphate is separated by fractional crystallization and the mother liquor is mixed with potassium sulphate when potash alum crystallizes out.

It is a white crystalline substance soluble in water. Its solution is acidic due to hydrolysis of aluminium sulphate. On heating it swells up due to removal of water of crystallization and on further strong heating it gives alumina.

The crystals of alums are made up of $[M(H_2O)_6]^{3+}$ $[M(H_2O)_6]^{3+}$ and SO_4^{2-}, i.e. each of the metal ion is surrounded by six water molecules Since the size of lithium ion is too small to have coordination number six hence it does not form alum. The monovalent cations are larger in size hence the water molecules are too far from these to be chemically bound to the metal ion. The trivalent cation being small, is chemically bound to the water molecules.

It is used as a mordant for dyes, as a tanning additive and as a water-proofing agent.

Aluminium sulphate, $Al_2(SO_4)_3$. It is obtained by the reaction of aluminium, its oxide or hydroxide in dilute sulphuric acid.

$$2Al + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2$$
$$Al_2O_3 + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2O$$

It is manufactured by the treatment of bauxite or china clay with boiling sulphuric acid.

$$Al_2O_3.2SiO_2.2H_2O + H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 2SiO_2 + 5H_2O$$

In this process silica remains as insoluble mass which is removed by filtration. The filtrate is concentrated to get its crystals, $Al_2(SO_4)_3.18H_2O$.

It is a white crystalline substance. It is soluble in water, the solution is acidic due to hydrolysis. On strong heating it decomposes into alumina.

$$Al_2(SO_4)_3\,18H_2O \longrightarrow Al_2(SO_4)_3 + 18H_2O$$
$$Al_2(SO_4)_3 \longrightarrow Al_2O_3 + 3SO_3$$

It is used in purifying sewage water, dyeing, calico printing, foamite fire, extinguishers, tanning of leather, water proof cloth and sizing of paper.

It is also used in the manufacture of alums.

Alums. Alums are the double salts with the general formula:

$$M_2^{I}SO_4.M_2^{III}(SO_4)_3.24H_2O$$

(where M^{I} =monovalent Na^+, K^+, Rb^+, Cs^+, NH_4^+, Tl^+ or Ag^+ and M^{III}=trivalent Al^{3+}, Fe^{3+}, Cr^{3+}, etc.)

Li^+ ion being too small, it does not enter into the crystal lattice of an alum. Some commonly used alums are:

Potash alum, $K_2SO_4, Al_2(SO_4)_3, 24H_2O$
Frerric alum, $(NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$
Chrome alum, $K_2SO_4.Cr_2(SO_4)_3.24H_2O$
Sodium alum, $Na_2SO_2.Al_2(SO_4)_3\ 24H_2O$

To prepare an alum, hot equimolar solutions of the two metal sulphates are mixed and the resulting solution is cooled to obtain the desired cystals.

Alums are used to purify water and as mordants in dyeing. They act as styptics to stop bleeding of small cuts (after shave cuts).

Amalgam. An amalgam is an alloy containing mercury. Amalgams may be solid or liquid solutions, intermetallic compounds or mixtures of a solid solution and an intermetallic compound.

Americium (At. no. 95). It was identified by Seaborg and others in 1944. It was synthesised by bombarding ${}_{92}{}^{238}U$ with high-speed alpha particles from a cyclotron and first producing a fairly long lived beta emitting isotope of plutonium, ${}_{94}{}^{241}Pu$, which decays to form the alpha-emitting isotope of Americium, ${}_{95}{}^{241}Am$ with a half-life of approx. 500 years. The nuclear reactions are—

$${}^{238}_{92}U + {}_{2}{}^{4}He \longrightarrow {}^{241}_{94}Pu + {}^{1}_{0}n \text{ (half-life of 13 years)}$$

$${}^{241}_{92}Pu \longrightarrow {}^{241}_{95}Am + e^{-} \text{ (half-life of 470 years)}$$

Ammonation. Ammonation is a type of solvation reaction in which liquid ammonia is used as a solvent and in which one or more ammonia molecules are attached to a solute species (a cation, an anion or a neutral molecule) by a chemical bond (H-bond or a coordinate bond). The products of solvation are called solvates and in the case of ammonation they are known as ammoniates. Solvation in water is called hydration and the products are known as hydrates. Formation of typical ammoniates is shown below:

$SO_3 + 2NH_3 \longrightarrow SO_3.2NH_3$	1 : 2 adduct
$SiF_4 + 2NH_3 \longrightarrow SiF_4.2NH_3$	1 : 2 adduct
$BF_3 + NH_3 \longrightarrow BF_3.NH_3$	1 : 1 adduct

Tendency to ammoniate decreases as the size of the ion increases.

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Ammonia. Traces of ammonia are persent in the atmosphere and are produced by the decay of organic matter and urine. Plants, animals, rock salts and mineral waters also contain small amounts of ammonium salts.

In the laboratory, ammonia is prepared by heating an ammonium salt with a base.

$$NH_4^+ + OH^- \longrightarrow NH_3 + H_2O$$

Generally, ammonium chloride is heated with dry slaked lime when ammonia evolved is passed through quick lime (for drying) and collected by the downward displacement of air. The other drying agents like P_4O_{10}, concentrated H_2SO_4 and anhydrous $CaCl_2$ cannot be used for drying ammonia because of the following reactions:

$$12NH_3 + P_4O_{10} + 6H_3O \longrightarrow 4\,(NH_4)_3PO_4$$
$$2NH_3 + H_2SO_4 \longrightarrow 2(NH_4)_2SO_4$$
$$8NH_3 + CaCl_2 \longrightarrow CaCl_2.\,8NH_3$$

Haber's process is generally used for the manufacture of ammonia. The process involves the direct combination of nitrogen and hydrogen under suitable conditions. The reaction is reversibe, exothermic and proceeds with a decrease in volume. Hence, in conformity with Le-Chatelier's principle, low temperature and high pressure should favour the formation of ammonia. In actual practice, an optimum temperature of 750 K and a pressure of 100-1000 atmospheres are employed. The reaction is further acclerated by the presence of finely divided iron (containing traces of molybdenum) catalyst.

$$N_2 + 3H \rightleftharpoons 2NH_3\ (\triangle H = -94\ \text{k Jmol}^{-1})$$

The Cyanamide process is also used for the manufacture of ammonia. In this process, nitrogen is reacted with calcium carbide at 1470 K. The resulting product known as nitrolim (mixture of calcium cyanamide and graphite) is hydrolysed with steam under a pressure of 3-4 atmospheres to yield ammonia.

$$CaC_2 + N_2 \longrightarrow CaCN_2 + C\ \text{(Nitrolim)}$$
$$CaCN_2 + 3H_2O \longrightarrow CaCO_3 + 2NH_3$$

During the manufacture of coal gas, ammonia is obtained as an important by product.

The colourless and pungent ammonia gas can be easily liquified and solidified. Its molecule is pyramidal and highly polar. Liquid ammonia is extensively hydrogen-bonded because of the high electronegativity of nitrogen. This additional bonding explains the exceptionally higher melting and boiling points of ammonia compared to those of the other hydrides. Hydrogen bonding seems to be responsible for the high solubility of ammonia in water.

Ammoniacal. A solution in aqreous ammonia.

Ammonolysis. Ammonolysis is a reaction in liquid ammonia which is similar to hydrolysis in aqueous medium. Just as in hydrolysis reactions, the concentration of H^+ or OH^- ions increases due to autoionization of water, in ammonolysis the concentration of either NH_4^+ or NH_2^- ions increases due to auto-ionization of ammonia. Consider the followiug reactions:

$$\text{Hydrolysis}\begin{cases} H_2O+H_2O \rightleftharpoons H_3O^+ + OH^- \\ CuSO_4+4H_2O \rightleftharpoons \underset{\text{(base)}}{Cu(OH)_2}+SO_4^{2-}+2H_3O^+ \end{cases}$$

$$\text{Ammonolysis}\begin{cases} NH_3+NH_3 \rightleftharpoons NH_4^+ + NH_2^- \\ SiCl_4+8NH_3 \rightleftharpoons \underset{\text{(base)}}{Si(NH_2)_2}+4NH_4+4Cl^- \end{cases}$$

In ammonolysis reactions, the atom or ion from the compound undergoing ammonolysis is replaced by$-NH_2$ or$=NH$ or $\equiv N$ group. For example, in excess of liquid ammonia the ammonolysis of $TiCl_4$ takes place in steps as:

$$TiCl_4 \xrightarrow{\text{liq. } NH_3} TiCl_3(NH_2) \xrightarrow{\text{liq. } NH_3} TiCl_2(NH_2)_2 \xrightarrow{\text{liq. } NH_3} TiCl(NH_2)_3 \xrightarrow{\text{liq. } NH_3} Ti(NH_2)_4$$

In case of organic halides with undergo slow ammonolysis at the boiling point of liquid ammonia, mixtures of primary, secondary and tertiary amines are formed.

$$RX+2NH_3 \longrightarrow RNH_2+NH_2X$$
$$RX+RNH_2+NH_3 \longrightarrow R_2NH+NH_4X$$
$$RX+R_2NH+NH_3 \longrightarrow R_3N+NH_4X$$

where X=Cl, Br, I, F, etc.

Alkali metal hydrides and oxides also undergo ammonolysis to give amides.

$$NaH+NH_3 \longrightarrow NaNH_2+H_2$$
$$Na_2O+2NH_3 \longrightarrow 2NaNH_2+H_2O$$

Amphoterism. A compound that dissolves both in acids and alkalis is said to be amphoteric in character. In an aqueous medium, zinc and alluminium hydroxides are amphoteric. In liquid ammonia, zinc amide also shows amphoteric behaviour. This is illustrated by the following reactions:

$$Zn(OH)_2+2HCl \xrightarrow{H_2O} ZnCl_2+2H_2O$$
$$Zn(NH_2)_2+2NH_4Cl \xrightarrow{\text{liq. } NH_3} ZnCl_2+4NH_3$$
$$Zn(OH)_2+2NaOH \xrightarrow{H_2O} Na_2ZnO_2+2H_2O$$
$$Zn(NH_2)_2+2NaNH_2 \xrightarrow{\text{liq. } NH_3} Na_2Zn(NH_2)_4 \text{ or } Na_2Zn(NH)_2+2NH_3$$

Anhydride. An anhydride is an oxide. By adding water to an anhydride, one can (at least in theory) produce a hydroxy compound which will be either an acid, a base, or an amphoteric compound. The corresponding oxides are therefore called acidic basic, or amphoteric oxides (anhydrides).

Annealing. It is the pocess of heating steel to a bright red heat and then cooling it slowly. By annealing steel becomes soft and pliable It wears better than wrought iron.

Antimony, (Latin *stabium*) **Sb.** A Group VA element of the 5th period of the Periodic Table of Elements, atomic number 51, atomic mass 121.75. One of the earliest known elements.

Properties Silvery brittle metal, m.p. 873K. Insoluble in HCl and H_2SO_4; oxidation states in compounds −3, +3, +5; at elevated temperatures, reacts with oxygen, halogens, sulphur, arsenic, and phosphorus; forms two oxides: $Sb_2O_3(Sb_4O_6)$, amphoteric, and Sb_2O_5. Acids react with metal (Zn, Al, etc.) antimonide to give stibine (hydrogen antimonide), SbH_3.

Ores Stibnite or atimonite (Sb_2S_3).

Extraction From stibnite.

Uses In alloys for the production of type metal, bearing metal (babbitt), the manufacture of semiconductors (AlSb, GaSb). Antimony compounds also have practical applications. In the organic synthesis $SbCl_3$ is used as catalyst and $SbCl_5$ as chlorinating agent; Sb_2O_2 is used in the rubber industry in medicine, in the production of glass, ceramics, and dyes.

Antimony hydride, stibine, SbH_3. It is obtained by the reduction of antimony trichloride by nascent hydrogen (zinc and hyro chloric acid) or by the reaction of magnesium antimonide and hydrochloric acid.

$$SbCl_3+6H\xrightarrow{Zn/HCl}SbH_3+3HCl$$

$$Mg_2Sb_2+6HCl\longrightarrow 3MgCl_2+2SbH_3$$

It is a colourless, poisonous gas with unpleasent smell. It is less soluble in carbon disulphide and ether. It is unstable and decomposes at room temperature with explosion.

$$2SbH_3\longrightarrow 2Sb+3H_2$$

It burns in air with a blue flame and forms white fumes of antimony trioxide.

$$4SbH_3+6O_2\longrightarrow Sb_4O_6+6H_2O$$

It forms black precipitate of silver stibnide with silver nitrate, which decomposes in the excess of silver nitrate.

$$SbH_3+3AgNO_3\longrightarrow Ag_3Sb+3HNO_3$$

$$2Ag_3Sb+6AgNO_3+3H_2O\longrightarrow 12Ag+Sb_2O_3+6HNO_3$$

Antimony pentachloride, $SbCl_5$ It is obtained by burning antimony in chlorine or by the action of chlorine on atimony trichloride.

$$2Sb+5Cl_2 \longrightarrow 2SbCl_5$$
$$SbCl_3+Cl_2 \longrightarrow SbCl_5$$

It is yellow fuming liquid with an unpleasant smell (b.p. 413 K, f.p. 275.39 K). It dissociates at its boiling pointas:

$$SbCl_5 \rightleftharpoons SbCl_3+Cl_2$$

It is hydrolysed in hot water to form antimony pentoxide.

$$2SbCl_5+5H_2O \longrightarrow Sb_2O_5+10HCl$$

It forms hydrated salts at low temperature as $SbCl_5.H_2O$ and $SbCl_5.4H_2O$.

Antimony powder. Antimony in the form of fine black powder is obtained by dissolving antimony trichloride in hydrochloric acid and pieces of zinc are added to the solution. The evolved nascent hydrogen reduces antimony trichloride to antimony.

$$SbCl_3+3H \xrightarrow{Zn/HCl} Sb+3HCl$$

The roasted ore is smelted in the presence of charcoal and sodium carbonte to get antimony.

$$Sb_4O_6+6C \longrightarrow 4Sb+6CO$$

Antimony tetroxide, Sb_4O_6. It is obtained by heating atimony trioxide in air or heating antimony pentoxide alone at red heat.

$$Sb_4O_6+O_4 \xrightarrow{675\text{ K}} 2Sb_2O_4$$
$$2Sb_2O_5 \xrightarrow[\text{heat}]{\text{red}} 2Sb_2O_4+O_2$$

It is white when cold and yellow when hot.
It is insoluble in water and acid.
It decomposes on strong heating.

$$2Sb_2O_4 \longrightarrow Sb_2O_6+O_2$$

It forms hypo-antimonates on fusion with alkalis.

$$Sb_2O_4+2KOH \rightarrow K_2Sb_2O_5+H_2O$$

Antimony trfluoride, SbF_3. It is obtained by dissolving antimony trioxide in hydrofluoric acid.

$$Sb_4O_6+12HF \longrightarrow 4SbF_3+6H_2O$$

Antimony trisulphide, Sb_2S_3. It is obtained by passing hydrogen sulphide gas through the solution of antimony trichloride in dilute hydrochloric acid.

$$2SbCl_3+3H_2S \longrightarrow Sb_2S_3+6HCl$$

It is an orange red coloured solid. It changes into greyish black at 475 K due to slight decomposition. It is soluble in concentrated hydrochloric acid, strong alkalis and yellow ammonium sulphide.

$$Sb_2S_3+6HCl \longrightarrow 2SbCl_3+3H_2S$$

$$Sb_2S_3+6NaOH \longrightarrow \underset{\text{sodium antimonite}}{Na_3SbO_3}+\underset{\text{sodium thioantimonite}}{Na_3SbS_3}+3H_2O$$

$$Sb_2S_3+3(NH_4)_2S+2S \dashrightarrow \underset{\text{ammonium thioarsenate}}{2(NH_4)_3SbS_4}$$

It is used in the manufacture of safety matches, red antimony, rubber and in fire works. Its mixture with sulphur and nitre is used for blue fire.

Argon. An inert colourless odourless monatomic element of the noble-gas group. It forms 0.93 per cent by volume of air. Argon is used to provide an inert atmosphere in electric and fluorescent lights and in welding.

Symbol: Ar; m.p. 83.8 K; b.p. 87.3 K; d. 1.78 kg m^{-3}.

Arsenic, [Greek *arsenikos*, strong, masculine] As. A Group VA element of the 4th period of the Periodic Table of Elements, atomic number 33, atomic mass 74.9216. Has one stable isotope, ^{75}As. Natural arsenic compounds were known to the ancients.

Properties Exists in several allotropic forms, the most stable one under usual conditions is metallic or grey arsenic. Arsenic derivatives are highly poisonous.

Reactions Usually occurs in compounds in the oxidation states +5, +3, —3. Undergoes oxidation to As_2O_3 when heated in the air. Gives metal arsenides on alloying with metals.

Ores The most important mineral is arsenopyrite, FeAsS.

Uses Free arsenic is of limited use in the production of certain alloys, e.g. in the manufacture of lead bullets. Arsenic compounds are widely applied in agriculture as means against vermins, in medicine.

Arsenic compounds. Arsenic trioxide (white arsenic), As_2O_3, is used as hide preservative, in the manufacture of glass and other arsenic compounds. Reacts with alkalis to give arsenites. Arsenic pentoxide, As_2O_5, gives arsenic acid, H_3AsO_4, in aqueous solutions. Arsenic acid salts are called arsenates. Arsenic hydride (arsine), AsH_3, is a colourless gas, smells like garlic, extremely poisonous. A large number of organoarsenic derivatives have been synthesized.

Arsenic hydride, Arsine, AsH_3. It is prepared by the reduction of arsenicus salts with nascent hydrogen (zinc and dilute sulphuric acid).

$$As_2O_3+12H\xrightarrow{Zn/H_2SO_4}2AsH_3+3H_2O$$

$$AsCl_3+6H\xrightarrow{Zn/H_2SO_4}AsH_3+3HCl$$

It can be prepared by the reaction of metal arsenides with dilute acids.

$$Zn_3As_2+6HCl\longrightarrow 2AsH_3+3ZnCl_2$$
$$Mg_3As_2+3H_2SO_4\longrightarrow 3MgSO_4+2AsH_3$$

The arsine obtained by these methods contain some impurities of hydrogen which can be removed by liquefying arsine at 173 K.

It is a colourless, extremely poisonous gas with garlic like smell.

It liquefies at 218 K and solidifies at 154 K (m.p. 159.5 K).

On heating (upto 505 K) it decomposes into arsenic and hydrogen. Black arsenic gets deposited in glass test tube to form metallic mirror (Marsh test).

$$2AsH_3 \longrightarrow 2As + 3H_2$$

It burns in air with bluish flame.

$$2AsH_3 + 3O_2 \longrightarrow As_2O_3 + 3H_2O$$

It acts as a reducing agent.

$$6KMnO_4 + 9H_2SO_4 + 5AsH_3 \longrightarrow 5H_3AsO_4 + 3K_2SO_4 + 6MnSO_4 + 8H_2O$$

$$K_2Cr_2O_7 + 4H_2SO_4 + AsH_3 \longrightarrow H_3AsO_4 + K_2SO_4 + Cr_2(SO_4)_3 + 3H_2O$$

$$6AgNO_3 + 3H_2O + AsH_3 \longrightarrow H_3AsO_3 + 6HNO_3 + 6Ag$$

It reacts with metals and metal oxides to form arsenides.

$$6Na + 2AsH_3 \longrightarrow 2Na_3As + 3H_2$$
$$3CuO + 2AsH_3 \longrightarrow Cu_3As_2 + 3H_2O$$

Arsenic pentachloride, $AsCl_5$. It is believed to be obtained by passing chlorine over heated arsenic trichloride.

$$AsCl_3 + Cl_2 \longrightarrow AsCl_5$$

Its existence is doubtful.

Other halides of arsenic may be obtained by the direct combination of respective elements.

Arsenic pentasulphide, As_2S_4. It is obtained as yellow precipitate by passing hydrogen sulphide gas through strongly acidic solution of an arsenate.

$$2Na_3AsO_4 + 6HCl + 5H_2S \longrightarrow As_2S_5 + 6NaCl + 8H_2O$$

It is also obtained by fusion of arsenic trisulphide and sulphur in the requisite quantities.

$$As_2S_3 + 2S \longrightarrow As_2S_5$$

It is soluble in alkali and sodium sulphide to form arsenate.

$$4As_2S_5+24KOH\longrightarrow 3K_3AsO_4+5K_3AsS_4+12H_2O$$
$$As_2S_5+3Na_2S\longrightarrow 2Na_3AsS_4$$

These arsenates decompose by acid to give precipitate of arsenic pentasulphide.

$$2Na_3AsS_4+6HCl\longrightarrow 6NaCl+3H_2S+As_2S_3$$

Arsenic pentoxide, As_2O_5. It is obtained by the oxidation of the arsenius oxide or by heating arsenic acid at 725 K.

$$As_2O_3+2Cl_2+2H_2O\longrightarrow As_2O_5+4HCl$$
$$As_2O_3+2HNO_3\longrightarrow As_2O_5+H_2O+N_2O_3$$
$$2H_3AsO_4\longrightarrow As_2O_5+3H_2O$$

It is a colourless, crystalline and deliquescent solid.
It is acidic in nature.

$$As_2O_5+3H_2O\rightarrow 2H_3AsO_4$$

It decomposes on heating upto 675 K.

$$As_2O_5+As_2O_3+O_2$$

It is an oxidizing agent.

$$As_2O_5+4HI\longrightarrow As_2O_3+2H_2O+2I_2$$
$$As_2O_5+2H_2S\longrightarrow As_2O_3+2H_2O+2S$$
$$As_2O_5+2Na_2SO_3\longrightarrow As_2O_3+2Na_2SO_3$$

Its sodium salt, $Na_2HAsO_4.12H_2O$ is used in calico printing and lead salt, $PbHAsO_4$ is used as a spray for fruit trees.

Arsenious acid, H_3AsO_3. Arsenious acid does not exist independently, but in aqueous solution it exists in two forms orthoarsenious acid, (H_3AsO_3) and meta arsenious acid ($HAsO_2$).

$$\begin{array}{ccccc} A_2sO_3+3H_2O & \rightleftharpoons & H_3AsO_3 & \rightleftharpoons & H_2O+HAsO_2 \\ & & \updownarrow & & \updownarrow \\ & & 3H^{+}+AsO_3^{3-} & & H^{+}+AsO_2^{-} \end{array}$$

Its salts are known as arsenites which may be either ortho arsenites, Na_3AsO_3, meta arsenites, $NaAsO_2$ or pyroarsenites $Na_4As_2O_5$ which are derived from the corresponding acids.

Arsenious acids and its salts act as reducing agents, e.g.

$$H_3AsO_3+I_2+H_2O \dashrightarrow H_3AsO_4+2HI$$

Artificial radioactivity. Many stable nuclei when bombarded by particles travelling at suitably high speed become unstable and start decaying giving new nuclear species. The radioactivity caused by such bombardment in stable nuclei is known as artificial radioactivity. For example when nitrogen is bombarded by α-particles, hydrogen and oxygen are produced, the change being represented as

$${}^{14}_{7}N+{}^{4}_{2}He \dashrightarrow {}^{17}_{5}C+{}^{4}_{1}H$$

Similar reactions are observed for many other elements and by many other bombarding particles.

Artificial transmutation. It means the conversion of one element into another, In 1919, Rutherford reported the first artificial transmutation. He discovered that when α-particles (from ${}^{214}_{82}Po$) pass through nitrogen gas, very fast potrons (${}^{1}_{1}H$) originate and the product oxygen is formed, i.e.

$${}^{14}_{7}N+{}^{4}_{2}He \longrightarrow {}^{17}_{8}O+{}^{1}_{1}H$$

In the reaction, the projectile (α-particle, in this case) forms a compound nucleus with the target (nitrogen). The compuund nucleus then rapidly ejects a subsidiary particle (proton) to give the product (oxygen).

In the following years, thousands of such transformations have been studied using different projectiles such as neutrons (${}^{1}_{0}n$), deuterons (${}^{2}_{1}H$), protons (${}^{1}_{1}H$),etc., in addition to α-particles. Projectiles which bear a positive charge are repelled by targets. Various accelerators, such as cyclotron and linear accelerator, are employed to impart sufficiently high kinetic energies to the positive projectiles to overcome the electrostatic repulsion of the targets,

Atomic bomb. As in an atomic pile, the atom bomb also utilises the chain reaction that develops on fission of ^{235}U, But in contrast to atomic pile where the chain reaction is controlled, the conditions are made favourable for its promotion in the atom bomb. The least amount of uranium with which the chain reaction is just possible is its critical mass; smaller lumps do not explode. But if small lumps, the added mass of which is greater than the critical, are suddenly brought together, a violent reaction sets in, resulting in an explosion. This is the principle of atom bomb. The atom bomb consists essentially of two separate means of ^{235}U (weighing a few pounds, each smaller than the critical mass but together exceeds the critical), kept separate from one another and enclosed in a shell of special material which serves as neutron reflector. When the bomb is to be fired, the two separate masses are brought together within about 1 millionth of a second by an ordinary explosive charge (also placed in a common outer shell together with the uranium pieces), and the atomic explosion results, releasing a huge amount of energy (comparable to that available from detonation of about 100,000 tons of T.N.T.). The temperature of atomic explosion would be several million degrees and pressure several million atmospheres. The fission is caused by fast neutrons in atom bombs. Plutonium-239 undergoes fission like ^{235}U and is also used in making atom bombs.

Atomic pile. The chain reaction of atomic fission is just maintained under controlled conditions in an atomic pile, i.e. the atomic pile is a controlled, self-sustaining nuclear reaction. Now, as we know, no chain reaction (which is based on capture of slow neutrons) develops in natural uranium, as the neutrons are absorbed by the ^{238}U nuclei. But if very pure natural uranium be distributed in small pieces at equal distances through a mass of graphite (which acts as a moderator), a chain reaction is developed. The atomic pile consists essentially of rods of extremely pure natural uranium inserted in a graphite block.

Aqua regia. A mixture of about three parts concentrated hydrochloric acid to one part concentrated nitric acid is known as aqua regia. It is a remarkable solvent (for both metals, such as gold and platinum, and salts, such as HgS) because it contains NO_3^-, a good oxidizing agent, and Cl^-, a good complexing agent.

Average life period. In fact the whole of the radioactive substance never disintegrates fully, however its concentration goes on decreasing with time. During the course of time, the instantaneous concentration of the radioactive substance is so small that it cannot be measured accurately. Thus we define the average life period (τ), in place of the total life period. The average life period 'τ' is related with the radioactive constant 'λ' as follows:

Average life period,

$$\tau = \frac{1}{\lambda}$$

But
$$\lambda = \frac{0.693}{t_{1/2}}$$

$\therefore$
$$\tau = \frac{1}{\frac{0.693}{t_{1/2}}}$$
$$= \frac{t_{1/2}}{0.693}$$
$$= 1.44 \times t_{1/2}$$

$\therefore$ Average life period = 1.44 × half-life period

B

Barium [Greek *barys*, heavy] **Ba.** A Group IIA element of the 6th period of the Periodic Table of Elements, atomic number 56, atomic mass 137.34. An alkaline earth metal. Discovered by Scheele in 1774.

Properties Soft silvery-white metal, m.p. 1123 K. An active metal, readily undergoes oxidation in the air, vigorously reacts with water to give barium hydroxide, reacts directly with many elements. In compounds, occurs in the +2 state.

Occurrence As barite, $BaSO_4$, witherite, $BaCO_3$.

Uses Barium and its alloys are used to absorb gases in electron tubes, barium oxide in the manufacture of cathodes. The most important barium compounds are barium peroxide, BaO_2 (catalysis, the preparation of H_2O_2 and bleaches), barium hydroxide, $Ba(OH)_2$ (absorption of CO_2), barium carbonate (the synthesis of other barium compounds, glass industry, enamels, glaze), barium chloride, $BaCl_2.2H_2O$ (rat and vermin poison, the manufacture of leather), barium sulphate, $BaSO_4$ (white pigment, strongly absorbs γ-rays, indicator in X-ray photography). Barium compounds turn flame green.

Barium carbonate ($BaCO_3$). It is a white insoluble salt that occurs naturally as the mineral witherite. Barium carbonate can be readily precipitated by adding an alkali carbonate to a barium salt solution. On heating it decomposes reversibly with the formation of the oxide and carbon dioxide.

$$BaCO_3 \rightarrow BaO + CO_2$$

It is used as a rat poison.

Barium chloride ($BaCl_2$). It is a white solid that can be prepared by dissolving barium carbonate in hydrochloric acid and crystallizing out the dihydrate ($BaCl_2 \cdot 2H_2O$). Barium chloride is used as the electrolyte in the extraction of barium, as a rat poison, and in the leather industry.

Barium hydrogencarbonate (Barium bicarbonate, $Ba(HCO_3)_2$). It is a compound that occurs only in aqueous solution. It is formed by the action of cold water containing carbon dioxide on barium carbonate, to which it reverts on heating.

$$BaCO_3 + CO_2 + H_2O \rightarrow Ba(HCO_3)_2$$

Barium hydroxide (Baryta, **$Ba(OH)_2$**). It is a white solid usually obtained as the octahydrate, $Ba(OH)_2.8H_2O$. Barium hydroxide is the most soluble of the group IIA hydroxides and can be used in volumetric analysis for the estimation of weak acids using phenolphthalein as an indicator.

Barium oxide (**BaO**). It is a white powder prepared by heating barium in oxygen or by thermal decomposition of barium carbonate. It has been used in the manufacture of lubricating-oil additives.

Barium peroxide (**BaO_2**). It is a dense off-white powder that can be prepared by carefully heating barium oxide in oxygen. Barium peroxide is used for bleaching straw and silk and in the laboratory preparation of hydrogen peroxide.

Barium sulphate ($BaSO_4$). It is a white solid that occurs naturally as the mineral barytes. Barium sulphate is very insolublein water and can be prepared easily as a precipitate by adding sulphuric acid to barium chloride, It is an important industrial chemical used as a pigment extender in surface coating compositions. It is also used in the glass and rubber industries.

Basicity (or protocity of an acid). It is the number of H^- ions furnished by a molecule of an acid. An acid may be classified according to its basicity or protocity. Thus, we may have monobasic or monoprotic acid (like HCl, HNO_3, etc.) dibasic or diprotic acids (like H_2SO_3, H_2CO_3, etc ,) and tribasic or triprotic acids (like H_3PO_4) as they liberate one, two and three H^+ ions respectively.

Basic salt. Refers to a compound intermediate between a normal salt and a hydroxide or oxide. The term is usually restricted to hydroxyhalides (such as Pb(OH)Cl, $Mg_2(OH)_3Cl_2$ $4H_2O$, and Zn (OH) F) and hydroxy-oxy slts (for example, $2PbCO_3$. $Pb(OH)_2$ $Cul(OH)_2.CuCl_2$, $Cu(OH)_2$, $CuCO_3$). These are essentially closely packed assemblies of OH^- with metal or halide ions in the octahedral holes. The hydroxy-oxy salts have more complex structures than those implied by the formulae.

Basic slag, 3 4 percent citrate soluble phosphorus pentoxide. Basic slag is obtained as a by product of steel industry. Since it has citrate soluble phosphorus, it is useful only in acidic soils where it may yield available phosphorus. Basic slag should be ground into very fine state of subdivision before application to soils. The availability of phosphorus is more under wetter soil conditions with higher amounts of organic matter. It is dark grey in colour. It must be added in heavy doses at least a month before sowing so that its slow action may be compensated.

Berkelium (At. No. 97). Berkelium, the eighth member of the actinide transition series and the fifth transuranic element was discovered in late 1949 by Seaborg and others. It was named in honour of Berkeley. It was synthesized by bombarding americium—241 with high speed alpha particles from the Berkeley cyclotron.

$$^{241}_{95}\mathrm{Am} + ^{4}_{2}\mathrm{He} \longrightarrow ^{243}_{97}\mathrm{Bk} + 2^{1}_{0}\mathrm{n} \quad \text{(Half-life of 4.6 h)}$$

A longer lived isotope, $^{245}_{97}\mathrm{Bk}$ has been synthesized by Seaborg and his co-workers in a similar reaction in which alpha particles are captured without neutron emmission.

$$^{241}_{95}\mathrm{Am} + ^{4}_{2}\mathrm{He} \longrightarrow ^{245}_{97}\mathrm{Bk} \text{ (Half life of 4.95 days)}$$

Berlin blue, Turnbull's blue. Berlin blue is formed in the reaction of $[\mathrm{Fe}^{2+}(\mathrm{CN})_6]^{4+}$ and Fe^{3+}, Turnbull's blue in the reaction of $[\mathrm{Fe}^{3+}(\mathrm{CN})]^{3+}$ and $\mathrm{Fe}.^{2+}$ Both products have practically the same composition,

$$\mathrm{Fe}^{2+} + [\mathrm{Fe}^{3+}(\mathrm{CN})_6]^{3-} \longleftrightarrow \mathrm{Fe}^{3+}[\mathrm{Fe}^{2+}(\mathrm{CN})_6]^{4-}$$

At a 1:1 mole ratio, a colloid solution of "soluble" Berlin blue is formed:

$$\left.\begin{aligned} &\mathrm{K}^+ + \mathrm{Fe}^{3+} + [\mathrm{Fe}^{2+}(\mathrm{CN})_6]^{4-} \rightleftarrows \\ &\mathrm{K}^+ + \mathrm{Fe}^{2+} + [\mathrm{Fe}^{2+}(\mathrm{CN})_6]^{3-} \rightleftarrows \end{aligned}\right\} \mathrm{K}[\mathrm{Fe}^{3+}\mathrm{Fe}^{2+}(\mathrm{CN})_6]$$

In the presence of excess Fe^{3+} the reaction

$$\mathrm{Fe}^{3+} + 3[\mathrm{Fe}^{3+}\mathrm{Fe}^{3+}(\mathrm{CN})_6]^{-} \rightarrow \mathrm{Fe}^{3+}[\mathrm{Fe}^{3+}\mathrm{Fe}^{2+}(\mathrm{CN})_6]_3$$

occurs, insoluble Berlin blue is precipitated. In the presence of excess Fe^{2+} the reaction

$$Fe^{2+} + 2[Fe^{3+}\,Fe^{2+}\,(CN)_6]^- \rightarrow Fe^{2+}[Fe^{3+}Fe^{2+}(CN)_6]_2$$

occurs; to give a precipitate of insoluble Turnbull's blue. Insoluble precipitates of both compositions are destroyed by solutions of alkalis.

Uses Berlin blue is used in the manufacture of oil dyes, enamel dyes, etc.

Beryl [Greek *beryllos*, sea-green gem]. A mineral, beryllium silicate, $Al_2Be_3Si_6O_{18}$.

Properties Vitreous luster, brittle, hardness 7.5-8 0. Unattacked by acids except for hydrofluoric acid.

Uses Source of beryllium and its salts, gem stone. Depending on colour, classified as beryl proper (greenish blue), aquamarine (transparent blue), heliodor (yellow), emerald (bright green), morganite (pink). Of these, emerald, aquamarine, and heliodor are used as jewelry.

Beryllium (First called glucinium, from Greek *glykys*, sweet) Be. A Group IIA element of the 1st period of the Periodic Table of Elements, atomic number 4, atomic mass 9.0122 includes one stable isotope, ^9Be. Discovered by Vauquelin in beryl (1798).

Properties A hard silvery-white metal, m.p. 1453 K. Beryllium metal and its compounds are strong poisons. In compounds occurs in the oxidation $+2$ state; slowly undergoes oxidation in the air with the formation of a protective BeO film, soluble in hydrochloric and sulphuric acids, reacts with alkalis. Beryllium oxide is a white powder insoluble in water, BeO. Beryllium hydroxide, $Be(OH)_2$, shows amphoteric properties.

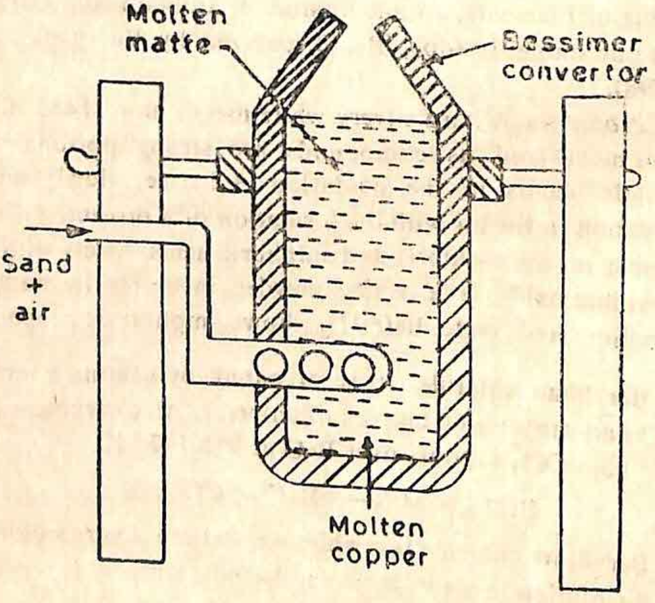
Beryllium chloride. It is prepared by heating a mixture of BeO and carbon in a current of chlorine. An alternative method is to pass CCl_4 vapours over BeO at 975 1975 K.

$$BeO + C + Cl_2 \longrightarrow BeCl_2 + CO$$

Beryllium chloride is a white, crystalline hygroscopic solid. Its dissolution in water is an exothermic process. It crystallizes as the tetrahydrate $BeCl_3.4H_2O$. Due to its covalent nature it also dissolves in alcohol, ether, acetone, etc. It forms a number of double salts.

Bessimerisation process. A molten mixture of cuprous sulphide and ferrous sulphide called 'matte' is formed by smelting of copper ore. This molten 'matte' is taken into a Bessemer converter. It is a pear shaped furnace which is made of steel plates that are lined inside with refractory bricks. The lining is of lime or magnesite. It is now mounted on turnions and is provided with tuyeres in the sides. A blast of air is passed through the molten 'matte'. Here FeS is oxidized to FeO and gets removed as $FeSiO_3$ (slag). When the whole of iron content has been removed as slag, cuprous suiphide gets partially oxidized into cuprous oxide. The air current is cut off now and the furnace is heated again.

The cuprous oxide reacts with the unchanged cuprous sulphide to yield impure copper. The molten copper so obtained is put into sand moulds. The molten copper has the tendency of dissolving gases (like SO_2). When it is solidified, the dissolved SO_2 is eliminated giving rise to a blistered apprearance. Such a copper is commonly called blister copper.



Beta particle. A beta particle is an electron which has been ejected, usually quite energetically, from the nucleus. Beta particles are more penetrating than alpha particles and are ejected typically from nuclei lying above the trough of stability.

Binding energy. The binding energy of an atomic nucleus is the energy required to pull the nucleons of the nucleus apart or the energy released by the hypothetical formation of the nucleus by the condensation of the individual nucleons.

The binding energy of a nucleus may be calculated from the difference between the sum of the masses of the constituent nucleons and the mass of the corresponding nucleus. The sum of the masses of the $^{35}_{17}Cl$ nucleus (17 protons+18 neutrons) is 0.320 amu greater than the actual mass of this nucleus. The energy equivalent of this mass is

$$0.320 \text{ amu} \times 931 \text{ MeV/amu} = 298 \text{ MeV}$$

For the purpose of comparison, the values are usually expressed in terms of binding energy per nucleon. The binding energy per nucleon in the case $^{35}_{17}Cl$ is

$$\frac{298 \text{ MeV}}{35 \text{ nucleons}} = 8.51 \text{ MeV/nucleon.}$$

The larger the binding energy per nucleon of a nucleus, greater is its stability. The largest values are the characteristic of the most stable nuclei.

Bioelements. These are the elements (metals and non-metals) essential for the structure of a living organism and its vital processes (metabolism, etc).

Bioligands. These are usually organic compounds, inorganic ions (F^-, Cl^-, I^-, SO_4^{2-}, NO_3^-) and neutral molecules (H_2O, O_2, CO_2, NH_3) which play a significant role in metabolic processes.

Biometals. Also called metals of life include metals forming ions with a noble-gas electron subshell (e.g. Na^+, K^+, Mg^{+2},

Ca^{2+}) and also elements with an 18-electron (Zn^{2+}) or incomplete 18-electron (Cu^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+}, Mo^{5+}, Mo^{6+}) subshell. The latter may change their oxidation state in the course of metabolic processes.

Bismuth. The Indian alchemists knew about bismuth and its compounds in the fourteenth century. But its characteristic properties were given by J.H. Pott in 1739. The name bismuth seems to be derived from the German word *weissmuth* meaning white matter. It occurs in small quantities in both free and combined states in nature. The important ores of bismuth are bismuth glance, Bi_2S_3; bismuth ochre or bismite Bi_2O_3 and bismuthile, $(BiO)_2CO_3$.

It is found in large quantities in Bolivia (South America). It is extracted from lead ores in Canada. There are also some sources of bismuth in India, China, Spain and Czechoslovakia.

The metal is obtained from native sources by the liquidation process. Bismuth flows down the tube in this process leaving behind the impurities.

The ores is concentrated by magnetic separation or washing and then roasted to get bismuth oxide. The roasted ore or bismite ore is then reduced by heating with carbon.

$$9Bi_2S_3+9O_2 \longrightarrow 2Bi_2O_3+6SO_2$$
$$(BiO)_2CO_3 \longrightarrow Bi_2O_3+CO_2$$
$$Bi_2O_3+3C \longrightarrow 2Bi+3CO$$

It is purified by fusing the impure bismuth with nitre when most of the impurities are oxidized to give pure bismuth.

It is a silvery white with reddish tinge, brittle metale (m.p. 544.3 K, b.p 1693 K, sp. gr. 9.8). It is a poor conductor of electricity and diamagnetic. The molten metal expands on solidification.

It forms bismuth trioxide on heating in air.

$$4Bi+3O_2 \longrightarrow 2Bi_2O_3$$

It reacts with sulphur and chlorine to form corresponding salts.

$$2Bi+3S \longrightarrow Bi_2S_3$$
$$2Bi+3Cl_2 \longrightarrow 2BiCl_3$$

Bismuth nitrate, $Bi(NO_3)_3\ 5H_2O$. It is obtained by dissolving the bismuth or its salts in dilute nitric acid.

$$2Bi + 8HNO_3 \longrightarrow 2Bi(NO_3)_3 + 2NO + 4H_2O$$
$$Bi_2O_3 + 6HNO_3 \longrightarrow 2Bi(NO_3)_3 + 3H_2O$$
$$Bi_2(CO_3)_3 + 6HNO_3 \longrightarrow 2Bi(NO_3)_3 + 3CO_2 + 3H_2O$$

It is a colourless, crystalline and deliquescent solid. It is hydrolysed in excess of water to form bismuth oxy-nitrate which is used for the treatment of dysentry and diarrhoea.

$$Bi(NO_3)_3 + H_2O \longrightarrow BiONO_3 + 2HNO_3$$

Bismuth pentoxide, Bi_2O_5. It is obtained by the reaction of potassium metabismuthate. $KBiO_3$, with dilute nitric acid which gives metabismuthic acid (scarlet red solid). On drying over concentrated sulphuric acid it changes into bismuth pentoxide,

$$KBiO_3 + HNO_3 \longrightarrow KNO_3 + HBiO_3$$
$$2HBiO_3 \longrightarrow Bi_2O_5 + H_2O$$

It is a brown powder and decomposes above 400 K.

$$Bi_2O_5 \longrightarrow Bi_2O_3 + O_2$$

It is amphoteric in nature.

$$Bi_2O_5 + 10HCl \longrightarrow 2BiCl_3 + 5H_2O + 2Cl_2$$
$$Bi_2O_5 + 3H_2SO_4 \longrightarrow Bi_2(SO_4)_3 + 3H_2O + O_2$$
$$Bi_2O_5 + 6KOH \xrightarrow{\text{fuse}} 2K_3BiO_4 + 3H_2O$$

Bismth sulphate , $Bi_2(SO_4)_3$. It is obtained by dissolving bismuth or its oxides or sulphides in hot and concentrated sulphuric acid. The product is crystallized by evaporation.

$$2Bi + 6H_2SO_4 \longrightarrow Bi_2(SO_4)_3 + 3SO_2 + 6H_2O$$
$$Bi_2O_3 + 3H_2SO_4 \longrightarrow Bi_2SO_4)_3 + 3H_2O$$
$$Bi_2S_3 + 3H_2SO_4 \longrightarrow Bi_2(SO_4)_3 + 3H_2S$$

It is a colourless, hygroscopic crystalline solid. It gives bismuthyl sulphate by partial hydrolysis.

$$Bi_2(SO_4)_3 + 2H_2O \longrightarrow (BiO)_2SO_4 + 2H_2SO_4$$

It forms white precipitate of basic sulphate $Bi_2O_3SO_3.2H_2O$ or $Bi_2(OH)_4SO_4$ with water.

Bismuth sulphide, Bi_2S_3. It is obtained by passing hydrogen sulphide gas through solution of bismuth salt in dilute hydrochloric acid.

$$2BiCl_3 + 3H_2S \longrightarrow Bi_2S_3 + 6HCl$$

It is a dark brown coloured solid and insoluble in water, sodium hydroxide and yellow ammonium sulphide unlike the sulphides of arsenic and antimony. It is soluble in concentrated mineral acids.

Bismuth trichloride,, $BiCl_3$. It is obtained by dissolving bismuth trioxide in hydrochloric acid.

$$Bi_2O_3 + 6HCl \longrightarrow 2BiCl_3 + 3H_2O$$

Anhydrous bismuth trichloride is obtained by passing chlorine over heated bismuth.

$$2Bi + 3Cl_2 \longrightarrow 2BiCl_3$$

It is a colourless crystalline solid (m.p. 506 K. b.p. 720 K). It is soluble in organic solvents.

It is hydrolysed in the excess of water to form white precipitate of bismuth oxychloride, which is dissolved in excess of hydrochloric acid.

$$BiCl_3 + H_2O \longrightarrow BiOCl + 2HCl$$
$$BiOCl + 2HCl \longrightarrow BiCl_3 + H_2O$$

Bismuth oxychloride is used as a white pigment under the name pearl white.

Bismuth trioxide, Bi_2O_3. It is obtained by strongly heating the metal or its nitrate and carbonate in air.

$$4Bi + 3O_2 \longrightarrow 2Bi_2O_3$$
$$Bi_2(CO_3)_3 \longrightarrow Bi_2O_3 + 3CO_2$$
$$4Bi(NO_3)_3 \longrightarrow 2Bi_2O_3 + 12NO_2 + 3O_2$$

It is a yellow fusible powder. It is amphoteric in nature but basic character dominates.

$$Bi_2O_3 + 6HCl \longrightarrow 2BiCl_3 + 3H_2O$$
$$Bi_2O_3 + 6NaOH \longrightarrow 2Na_3BiO_3 + 3H_2O$$

It is oxidized to bismuth tetroxide (scarlet red solid) by chlorine water.

$$Bi_2O_3+Cl_2+H_2O \longrightarrow Bi_2O_4+2HCl$$

Blast furnace. A furnace for producing iron from iron(III) oxide. A mixture of the ore (haematite) with coke and a flux is heated by pre-heated air blown into the bottom of the furnace. The flux is often calcium oxide (from limestone). Molten pig iron is run off from the bottom of the furnace.

Bleaching powder. Bleaching power, $CaOCl_2$ is obtained by passing dry chlorine over dry slaked lime, $Ca(OH)_2$ at 303-311 K.

$$\underset{\text{slaked lime}}{Ca(OH)_2}+Cl_2 \longrightarrow \underset{\text{bleaching powder}}{CaOCl_2}+H_2O$$

It is a yellowish white powder and gives a strong smell of chlorine. In presence of small amount of dilute acid, it can act as an oxidizing and bleaching agent. On treatment with an excess of a dilute acid or even corbon dioxide, bleaching powder liberates whole of its chlorine.

$$CaOCl_2+2H^+ \longrightarrow Ca^{2+}+H_2O+Cl_2$$
$$CaOCl_2+CO_2 \longrightarrow CaCO_3+Cl_2$$

The chlorine liberated on treatment of bleaching powder with acid is called available chlorine. A good sample of bleaching powder contains 35-38% of available chlorine.

Bleaching powder is mainly used for bleaching cotton, linen, jute and wood pulp. It is also used as a disinfectant and germicide for sterilizing water.

Bone meal. Ground animal bones, used as a phosphorus fertilizer (contains 29 to 34% P_2O_5).

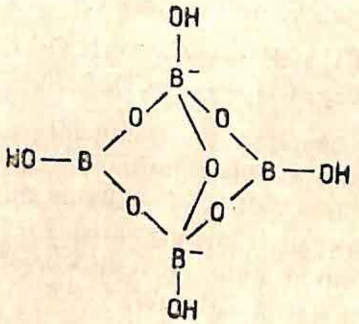
Borates. Metal salts of tetraboric acid, $H_2B_4O_7$, or metaboric acid, HBO_2. Occur in nature, e.g. borax, $Na_2B_4O_7.10H_2O$. Calicum borate is used in the manufacture of ceramics, zinc borate in the textile industry.

Borax (sodium tetraborate) $Na_2B_4O_4 \cdot 10H_2O$. A natural boron mineral.

Properties Transparent crystals, fully lose water at 675 K. Undergoes hydrolysis in water solutions to give an alkaline reaction; reacts with many metal oxides with the formation of coloured compounds (beads).

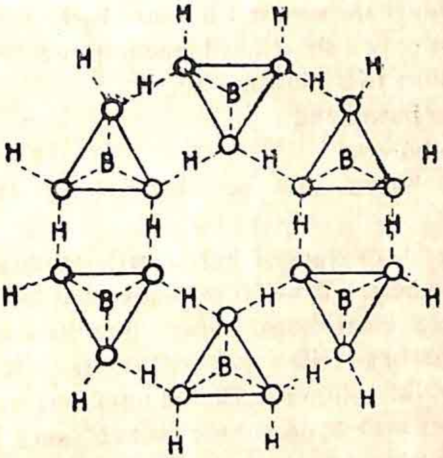
Uses The manufacture of enamels, optical and coloured glasses, as a flux in soldering, in the paper and pharmaceutical industries. Also employed as a disinfectant, a preservative. In the analytical chemistry, serves as a standard substance for the determination of concentrations of solutions of acids and for other purposes.

In borax, $Na_2B_4O_7.10H_2O$, two boron atoms are in triangular and two boron atoms are in tetrahedral geometry. The ion is $[B_4O_5(OH)_2]^{2-}$, the remaining eight water molecules are associated with the two sodium ions. Hence the borax may be formulated as $Na_2[B_4O_5(OH)_4].8H_2O$.



Bordeaux mixture. A mixture of slaked lime and copper sulphate solution. Used as a fungicide.

Boric acid (Orthoboric acid) H_3BO_3. A weak acid (colourless) odourless scales; found in nature (mineral sassolite, in hot and mineral springs). Used as boric fertilizer, as a disinfectant (medicine), for the preparation of buffer solutions (laboratory).



Hydsogen-bonded structure of orthoboric acid.

Boron. It is a hard brittle metalloid element of Group IIA. of the Periodic Table. It has the electronic structure $ls^2 2s^2 2p^1$. Boron is of low abundance (0.0003%) but the natural minerals occur in very concentrated form as borax ($Na_2B_4O_7$. $10H_2O$) and colemanite ($Ca_2B_6O_{11}$).

The element is obtained by conversion to boric acid followed by dehydration to B_2O_3 then reduction with magnesium. High-purity boron for semiconductor applications is obtained by conversion to boron trichloride, which can be purified by distillation, then reduction using hydrogen. Only small quantities of elemental boron are needed commercially; the vast majority of boron supplied by the industry is in the form of borax or boric acid.

As boron has a small atom and has a relatively high ionization potential its compounds are predominantly covalent; the ion B^{3+} does not exist.

Boron does not react directly with hydrogen to form boron hydrides or 'boranes' but the hydrolysis of magnesium boride does produce a range of boranes such a B_4H_{10}, B_5H_9, and B_9H_{10}. Thermal decomposition of these higher boranes produces, among other things the simplest borane, B_2H_6 (diborane). The species 'BH_3' is only a short lived reaction intermediate.

Boron exhibits two allotropic forms:

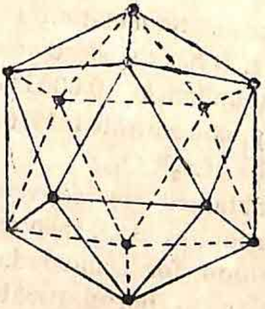
Amorphous boron and

Crystalline boron.

Crystalline boron can be obtained by the following methods.

By passing a mixture of boron tribromide and hydrogen over electrically heated filament of tungsten at 1475 K.

By dissolving amorphous boron in molten aluminium at 1800 K. On cooling yellow coloured crystals are obtained on the surface of aluminium. The aluminium is removed by boiling the mass with hydrochloric acid and very hard crystals of boron are left behind. It is believed that crystalline boron so obtained is not pure boron, it is a aluminium-boron compound like AlB_{12}.



●= Boron

The crystalline boron contains clusters of boron atoms situated at the corners of a nearly regular icosahedron. This basic B_{12} unit exists in many boron containing compounds.

Bromides. Compounds of bromine and metals, salts of hydrobromic acid such as sodium bromide, NaBr, and silver bromide, AgBr.

Bromine [Greek *bromos*, stench] Br. A Group VII A element of the 4th period of the Periodic Table of Elements, atomic number 35, atomic mass 79.904; natural bromine contains two stable isotopes, ^{79}Br (50.6%) and ^{81}Br (49.4%). Discovered by Balard in 1826.

Properties Heavy, dark, reddish-brown liquid, with a strong disagreeable odour. Solid bromine forms bright red crystals with metallic glitter m.p. 264 7 K, b.p. 331.8K. Soluble in many organic solvents; aqueous solutions of bromine are called bromine water. Valence −1 (bromides, KBr), +1 (NaBrO), +3 ($NaBrO_2$), +5 (bromates, $KBrO_3$): belongs to the halogen family, less active than chlorine but more so than iodine. Does not react with oxygen directly. Combines with hydrogen to give hydrogen bromide, HBr, whose aqueous solutions are called hydrobromic acid. Bubbling of chlorine through bromine water results in the formation of bromic acid.

$$5Cl_2 + Br_2 + 6H_2O = 2HBrO_3 + 10HCl$$

Bromic acid salts, bromates, are stable under usual conditions, show oxidizing action.

Uses The production of bromide salts and various organobromine derivatives. Bromine and its compounds are used in the synthetic organic chemistry, photography, medicine (sedatives). Bromine and bromine water are employed in chemistry as oxidizing agents.

Bronze. It is an alloy with copper as the major component. Depending on the second base component the term is used with reference to tin, aluminium, beryllium, lead, manganese, silicon, and other alloys, "bronzes". Bronzes have good mechanical properties. Bronze for bearings contains 89.5% Cu, 10%, Sn, and 0.5% Pb; bronze for gears 90% Cu and 10% Sn. Bronzes are used in the manufacture of details of mechanisms, for casting works of art, etc.

Bromine pentafluoride, BrF_5. It is prepared by actionof bromine on excess of fluorine.

$$Br_2+5F_2 \rightarrow 2BrF_5$$

It is colourless liquid (b.p. 314 K). It reacts very violently, hence it is diluted with nitrogen for the preparation of fluorides.

Bromine trifluoride, BrF_3. It is prepared by mixing bromine vapour and fluorine in a steam of nitrogen or by the action of chlorine trifluoride or bromine at 283 K.

$$Br_2+3F_2 \rightarrow 2BrF_3$$
$$Br_2+2ClF_3 \rightarrow 2BrF_3+Cl_2$$

It is a colourless fuming liquid (b.p. 400 K). It ionizes as:

$$2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$

It is a useful fluorinating agent, e.g.

$$6M+2BrF_3 \rightarrow 6MF+Br_2$$
$$3MCl+BrF_3 \rightarrow 3MF+BrCl_3$$
$$KF+BrF_3 \rightarrow KBrF_4$$
$$SbF_3+BrF_3 \rightarrow SbBrF_6$$
$$3SiO_2+4BrF_3 \rightarrow 3SiF_4+2Br_2+3O_2$$

C

Cadmium. Cadmium, a versatile metal, was once a metal of neglect but is now gaining importance. It is a rare element. Estimate of its occurrence in the earth's crust ranges from 0.1 to 0.2 ppm making it the sixty seventh element in order of abundance.

The crystal abundance of cadmium is somewhere between 0.1 to 0.5 ppm inspite of several cadmium minerals. Cadmium is almost invariably recovered as a by-product from the processing of zinc, lead and copper ores. There is no possibility of obtaining this metal from primary sources at least in foreseable future.

In non-polluted areas the cadmium concentration in soil will usually be less than 1 mg/kg. Sewage sludge may contain 100 mg cadmium/kg dry weight.

Cadmium concentrations in non-polluted natural waters usually are lower than 1 μg/L. Cadmium concentrations up to 16 mg/kg have been reported in fruit juices. Regular drinkging water usually does not have concentration of cadmium exceeding 5 μg/L. Sea water contains between 0.04 and 0.3 μg/L.

A wide range of cadmium concentrations in food stuffs has been reported from various countries. Different results from different investigators analyzing the same types of food in the same area can be explained in some cases by inadequate and unsuitable analytical methods. When data from reliable analysis performed in several countries are considered, the following concentrations (mean values mg/kg wet weight) result:

Beaf meat	0.03-0.06
Beef kidney	0.2-1.6
Fish meat	0.01-0.2
Wheat grains	0.01-0.15
Rice (USA and Hungry)	0.03-0.04
White bread	0.02-0.16
Milk	0.0002
Potatoes	0.001-0.09

These values have been obtained in areas generally believed to be uncontaminated by cadmium.

Annual averages in larger cities of the USA ranged from 0.006-0.036 μg/m³. In European countries urban values of 0.002-0 05 μg/m³ have been reported. In nonurban areas lower values were found, 0.001-0.003 μg/m³. Higher values, weekly means of 0.2-06 μg/m³ have been recorded around certain cadmium emittingindustries.

Smoking tobacco may be an important route of exposure. Smoking one cigarette, generally containing 1-2 μg cadmium, results in the inhalation of about O. 1−0.2 μg of the metal.

In blood, 'normal' levels in nonsmokers are generally below 1 μg/L, whereas considerably higher values, up to 7.6 μg/1, have been found in smokers. In urine 'normal' levels will also vary with age, area and smoking habits, generally being 1<μg/g creatinine, although 1-2 μg/g creatinine has been reported.

Cadmium and its compounds have been put to variety of uses in the industrial and consumer fields. Cadmium pigments, based on cadmium sulphide and cadmium sulphoselenide, can be produced in a range of brilliant shades of yellow, orange, red and marron. Most cadmium pigments are used in plastics, glasses, ceramics and vitreous enamels. Cadmium has extensive use in alloys. It is an important constituent of brazing and law melting alloys in bearing, solders and as a hardener for copper. In India railways consume this metal more as copper-cadmium (1% Cd) catenary alloy for electrification projects. Another major use of this metal in our country is in the electronics industry, lead acid batteries and ornament industries. Cadmium-bearing stabilizers are used to retard the degradation of polyvinyl chloride (PVC) on exposure to heat and sunlight. Like zinc, cadmium coating can be applied to steel to protect it from corrosion. For the same reason cadmium can be plated on brass, copper and aluminium and is particularly useful for components which are likely to be exposed to marine conditions, automabiles electrical and electronic parts, makers in the field of transport, the aerospace and ship-building industries. This metal is also used in the manufacture of nickel-cadmium batteries which are widely used for standby and emergeney power in hospitals, telephone exchanges, computer installations and offices. The use of cadmium sulphide for direct conversion of sunlight into electricity is an exciting application. Photovoltaic systems provide energy for lights, pumps and essential equipment like T.V. transmitters. The average amount of cadmium sulphide required for a solar cell is only few milligrams (≃25 microns), according to N.P.L., Delhi (India) report.

Emission spectroscopy has earlier displayed varying sensitivity and accuracy for cadmium. Modern equipment seems to ensure accurate analysis of about 50 ng. Destructive neutron activation analysis is regarded as an accurate method, but has not been widely used for cadmium. It has not yet been possible to detect normal levels in liquids such as urine with this method. In vivo determination of cadmium in liver by neutron activation was first described by Biggin et. al. In cadmium-exposed workers it was possible to demonstrate elevated liver levels of cadmium. The sensitivity has been increased and at present about 16 μg Cd/g wet weight in kidney and 1.8 μg Cd/g wet weight in liver can be detected. The radiation dose from one measurement is low. Further development of this method has brought about portable equipment for field use.

Atomic absorption spectrophotometry is the most common method for the determination of cadmium to date. By flameless AAS methods about 5 μg/kg can be accurately determined in food stuffs and even lower levels can be determined in urine and blood. However, interference of salts (e.g. Na salts), may cause inaccuracies if appropriate precautions are not taken. In blood, values well below 1μg/L have been accurately determined.

Published data have been based on inadequate methods of analysis. Errors, with values 10-100 times higher have been seen with regard to both emission spectroscopy and atomic absorption spectrophotometry.

Though ASS method is very convenient from the analyst's point of view but the accessibility of the instrumental facility to a common analyst/chemist becomes a hurdle in the choice and one looks for some alternate instrument and method. Spectrophotometric methods then become the methods of choice. Spectrophotometric procedures are popular, commonly employing dithizone regent to develope pink (520 nm) colour.

Calcium [Latin *calx*, *calcis*, lime] **Ca.** A Group IIA element of the 4th period of the Periodic Table of Elements, atomic number 20, atomic mass 40.08. An alkaline earth metal. Natural calcium compounds such as limestone, marble, gypsum, and also lime produced by the calcination of limestone have been used as building materials from ancient times. Calcium metal was first prepared by Davy in 1808.

Properties A silvery white metal, the oxidation state in compounds +2. Calcium metal is very reactive; it is a strong reducing agent, at elevated temperatures displaces almost all metals from their oxides, sulphides, and halides. At room temperature, readily reacts, with oxygen to give CaO which combines with water with the formation of a strong base, $Ca(OH)_2$. Vigorously reacts with acids to release hydrogen, reacts with halogens and dry hydrogen with the formation of calcium together with graphite yields calcium carbide, CaC_2.

Occurrence Found in sedimentary rocks and in various minerals; the chief ores are limestone and chalk.

Extraction By electrolyzing molten $CaCl_2$ or reducing calcium oxide with aluminium metal under vacuum and elevated temperature:

$$6CaO+2Al \rightarrow 3Ca+3CaO.Al_2O_3$$

Uses Pure metal used as a reducing agent for the preparation of Cs, Rb, Cr, U, Zr, Th, and V metals from their compounds; for oxidizing steels calcium alloys with lead are used to reduce friction. Calcium minerals have found wide applications; limestone is used in the manufacture of lime ash, cement, silicate bricks, and as a building material; it is also employed in metallurgy (flux), in the chemical industry (the production of calcium carbide, soda, caustic soda, chlorinated lime, fertilizers), in the manufacture of sugar and glass. Chalk, marble, Iceland spar (calcite), gypsum, fluorite, etc. are also important materials.

Calcium carbide, CaC_2. It is manufactured by heating a mixture of lime and coke powder at about 2275 K in an electric furnace.

$$CaO+C_3C \dashrightarrow CaC_2+CO$$

The furance is made of fine clay bricks and lined with carbon on the inner side and a thick layer of graphite at the bottom, which acts as one of the electrodes. The second electrode is fitted in the centre. On heating the mixture molten carbide is obtained at the bottom and is periodically tapped out. It is cooled to solidify and then broken into pieces.

It is colourless crystalline solid when pure. The commercial product is hard like stone with grey colour due to impurities. It decomposes water to form acetylene.

$$CaC_2 + 2H_2O \dashrightarrow Ca(OH)_2 + C_2H_2$$

It is heated with nitrogen at 1275 K to form calcium cyanamide.

$$CaC_2 + N_2 \dashrightarrow CaCN_2 + C$$

It is chiefly used for the preparation of acetylene in acetylene lamps. It is used in the manufacture of calcium cyanamide, an important fertilizer. It is used as a reducing agent.

Calcium chloride, $CaCl_2$. It is obtained as a by product in the Solvay ammonia process. It can also be prepared by the reaction of hydrochloric acid on calcium, calcium carbonate or oxide. The product is a syrup which on crystallization gives hexahydrate, $CaCl_2.6H_2O$. Anhydrous calcium chloride is obtained on heating.

$$CaCl_2.6H_2O \xrightarrow{473\ K} CaCl_2.2H_2O \xrightarrow{1050\ K} CaCl_2$$

It is a white solid, highly hygroscopic and deliquescent substance. It is soluble in water and alcohol. Since it forms coordination compounds with methanol and ammonia such as $CaCl_2.4CH_3OH$ and $CaCl_2.8NH_3$ respectively, it cannot be used for drying these substances.

It is used as drying agent for gases and liquids; as an antifreeze for cement. It is used in making freezing mixture and in refrigeration and air conditioning. It is also used in dyestuffs, fire proofing, dust laying and road making.

Calcium compounds. Calcium arsenate, $Ca_3(AsO_4)_2$, poisonous, used as an insecticide; calcium arsenite, $Ca(AsO_2)_2$, used against locust and rodents (has a strong burning action on plants, poisonous); calcium hydride, CaH_2, a reducing agent (in organic chemistry, metallurgy); calcium chloride, $CaCl_2$, absorbs moisture, used in medicine; calcium carbonate, $CaCO_3$, a filler for paper, rubber, linoleum; natural $CaCO_3$ and calcium sulphate, $CaSO_4$, are used as building materials; calcium phosphates (neutral, $Ca_3(PO_4)_2$, monohydro, $CaHPO_4$, and dihydro, $Ca(H_2PO_4)_2$, phosphates) are used in the manufacture of ceramics and glass, in dentistry (toothpaste), as phosphorus fertilizers, as soft abrasives; calcium cyanamide, $CaCN_2$, is a nitrogen fertilizer, also used for stripping plants of leaves before harvesting and as a weed-killing agent; calcium hypochlorite, $Ca(ClO)_2$, is employed for bleaching fabrics and cellulose, and as an oxidizer in chemical processes.

Calcium cynamide, $CaCN_2$. It is also known as nitrolim. It is manufactured by heating the finely powdered calcium carbide in the presence of nitrogen at 1275 K in an electic furance for about 30 hours.

$$CaC_2+N_2 \longrightarrow CaCN_2+C, \qquad \Delta H=-304 \text{ kJ}$$

The calcium cyanamide is obtained in the form of big pieces of stone, which are broken and crushed into powder form when it is used as a fertilizer, calcium carbide should not be more than 0.1%. The excess of calcium carbide is removed by spraying water on the product, which decomposes calcium carbide.

It is white in colour, moderately soluble in water. It subiimes at 1575 K It reacts with water to give cyanamide which on heating with water to 345 K changes into urea and finally into ammonia.

$$CaCN_2+2H_2O \longrightarrow Ca(OH)_2+H_2N.CN$$
$$H_2NCN+H_2O \longrightarrow NH_2CONH_2$$
$$H_2N.CO.NH_2+H_2O \longrightarrow CO_2+2NH_3$$

It is decomposed by steam to give ammonia.

$$CaCN+3H_2O \longrightarrow CaCO_3+2NH_3$$

It is used as a nitrogenous fertilizer and as a source of ammonia.

Calcium metaphosphate, $Ca(P_3O)_2$, 63% citrate soluble P_2O_5. The availability of phosphate in calcium metaphosphate is subject to acidic conditions of soil, as it contains only citrate soluble phosphate. It is a high grade fertilizer containing 63 per cent P_2O_5. The reaction involved in its manufacture is given below:

$$[Ca_2(PO_4)_2]_3CaF_2 + 7P_2O_5 + H_2O \rightarrow 10Ca(PO_3)_2 + 2HF$$

rock phosphate   phosphorus pentoxide   calcium metaphosphate

Calcium oxide, CaO. It is also known as quick lime. It is prepared by heating lime stone at 1075 K in specially designed kilns.

$$CaCO_3 \longrightarrow CaO + CO_2$$

It is white porous solid (m.p. 2845 K). It gives brilliant white light (lime light) when heated in an oxy-hydrogen flame. It gives a hissing sound and becomes very hot when water is added to it. This process is known as slaking of lime and the product, i.e. fine powder is called slaked lime.

$$CaO + H_2O \longrightarrow Ca(OH)_2 + 63 \text{ kJ}$$

The paste of lime in water is called milk of lime while the filtrate is called lime water. Chemically both are calcium hydroxide.

Calcium oxide is basic is nature hence reacts with oxides of the non-metals to form salts.

It is used in laboratory for drying gases and alcohol, for preparation of ammonia and soda lime.

It is used for the manufacture of cement, mortar, glass and calcium chloride. Slaked lime is used for the manufacture of bleaching powder, basic calcium nitrate, sodium hydroxide and sodium carbonate. It is used in lime light.

Calcium phosphate, $Ca_3(PO_4)_2$. It is prepared by the reaction of soluble phosphate with an alkaline solution of a calcium salt.

$$3CaCl_2 + 2NH_4OH + 2Na_2HPO_4 \longrightarrow Ca_3(PO_4)_2 + 2NH_4Cl + 4NaCl + 2H_2O$$

It is a white powder sparingly soluble in water. It reacts with phosphoric acid to form calcium dihydrogen phosphate.

$$Ca_3(PO_4)_2 + 4H_3PO_4 -- 3Ca(H_2PO_4)_2$$

It is used in tooth pastes. Calcium dihydrogen phosphate is a constituent of baking powder.

Calcium sulphate, $CaSO_4$. In nature it occurs as gypsum, $CaSO_4.2H_2O$ and anhydrite $CaSO_4$. It can be prepared by the action of of sulphuric acid on the solution of calcium salt.

It is sparingly soluble in water and solubility increases upto 313 K and decreases after this temperature. Gypsum loses 75 per cent water on heating at about 325 K to give plaster of Paris $CaSO_4.\frac{1}{2}H_2O$ or $2CaSO_4.H_2O$. Plaster of Paris sets to a hard mass when a paste with water is made, which expands with hardening. This final product of setting is $CaSO_4.2H_2O$.

$$2CaSO_4.2H_2O \dashrightarrow 2CaSO_4.H_2O + 3H_2O$$
$$2CaSO_4.H_2O + 3H_2O \longrightarrow 2CaSO_4.2H_2O.$$

On account of this property it is used in surgery for setting broken or dislocated bones. It is also used in making casts for statues, toys, etc.

It is used in the preparation of plaster of Paris. Gypsum is used in manufacture of cement, in agriculture and for impregnating filter papers.

Calgon. A substance usually added to detergents to remove unwanted chemicals that have dissolved in water and would otherwise react with soap to from a scum. Calgon consists of complicated polyphosphate molecules, which asorb dissolved calcium and magnesium ions. The metal ions become trapped within the Calgon molecules.

Caliche. An impure commercial from of sodium nitrate, $NaNO_3$

Californium (At. No. 98). The sixth transuranic element was discovered in 1950. It was named Californium in honour of the university and state where the work was done. The element was produced by bombarding microgram amounts of curium-242 with 35-meV alpha particles. The isotope to be identified was ^{244}Cf with a half-life of 45 minutes.

$$^{242}_{96}Cm + ^{4}_{2}He \longrightarrow ^{244}_{98}Cf + 2^{1}_{0}n \text{ (half-life of 45 minutes)}$$

Less energetic alpha particles produce a longer-lived isotope, ^{246}Cf with a half-life of 35.7 hours.

Carbides. Compounds of carbon with less electronegative elements are called carbides. The properties of the carbides depend upon the nature of linkage. These can be classified as:

Ionic or salt like carbides,
Covalent carbides,
Interstitial or metallic carbides.

Carbon [Latin *carbo, carbonis*, coal] **C.** A Group IVA element of the 2nd Period of the Periodic Table of Elements, atomic number 6, atomic mass 12.01115, contains two stable isotopes, ^{12}C (98.9 per cent) and ^{13}C (1.1 per cent). In 1961, 1/12 of the mass of an atom of $^{12}_{6}$C was adopted as the united atomic mass unit by the International Union of Pure and Applied Physics and the International Union of Pure and Applied Chemistry.

Properties Exists as several allotropic forms, e.g. diamond, graphite. The oxidation states in compounds +4 and, less frequently, +2 and + 3. Unreactive under usual conditions, but shows a high reactivity at elevated temperatures, especially in the amorphous state. The chemistry of carbon has been developed into a separate branch of study, the organic chemistry.

Occurrence Carbon compounds are the major constituents of all organic substances and the products of their decomposition.

Uses As an alloying element (steel, pig iron), as a material for electrodes, crucibles, in the manufacture of gunpowder, in smelting metals from their ores (coke), as an adsorbent (activated carbon), in the chemical industry. The ^{14}C isotope is used as a radioactive tracer.

Carbonate. A salt or ester of carbonic acid, H_2CO_3. Salts can be neutral and contain the CO_3^{2-} anion and acid (contain HCO_3^-). Alkali metal, ammonium, and thallium neutral carbonates are only soluble; their solutions are basic because of the hydrolysis. Calcium, barium, strontium, ane lead neutral carbonates have very low solubilities; all acid metal carbonates are soluble in water. Acid carbonates give neutral salts upon heating:

$$2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$$

Neutral carbonates are widely distributed in nature, e.g. calcite, $CaCO_3$ magnesite, $MgCO_3$, siderite, $FeCO_3$, witherite, $BaCO_3$, etc. Calcium, magnesium, barium, etc. carbonates are used in building, in the chemical in industry, in optics, etc. Soda (Na_2CO_3 and $NaHCO_3$) is extensively used in industry and household. Acid carbonates play an important role being buffer substances maintaining blood's pH at a constant level.

Carbon black. An amorphous form of carbon, the product of incomplete combustisn or thermal destruction of hydrocarbons. An excellent filler for rubber. Used in large amounts as a black pigment in polygraphy, in the manufacture of lacquers and dyes. Finely divided forms of amorphous silicon dioxide are used as a white sabstitute for carbon black; they are manufactured by the reaction of gaseous silicon tetrachloride with water vapour, and used as fillers for rubber, especially silicone rubber, in the manufacture of various lubricants, dyes, and lacquers.

Carbon dating. Carbon dating is a method of finding the age of a plant or a animal which died thousands of years ago. It was given by an American scientist W.F. Libby. This method is based on finding the radioactivity of radioactive carbon which is present in all the living objects. Radioactive carbon (^{14}C) is being constantly formed by the cosmic rays in the upper atmosphere. Neutrons produced by the cosmic rays bombard nitrogen atoms of the atmosphere resulting in the formation of radioactive carbon (^{14}C). This can be expressed in the form of an equation,

$${}^{1}_{0}n + {}^{14}_{7}N \longrightarrow {}^{6}_{14}C + {}^{1}_{1}H$$

The radioactive carbon (^{14}C) so formed combines with oxygen to form radioactive carbon dioxide (CO_2). This gas so formed is gradually mixed in the atmosphere and is absorbed by the living plants. These plants in turn are consumed by animals. This way ^{14}C enters the animal system. In short, we can surely say that all living objects have a certain amount of ^{14}C present in them.

The ratio of ^{12}C to ^{14}C remains constant as long as the plant lives (i.e. keeps growing). As the plant stops growing, the ratio of ^{14}C to ^{12}C decreases at a definite rate with time. ^{12}C is present in all objects, dead or living. The half-life of ^{14}C is 5568 years. Therefore, after a lapse of 5568 years of the death of the living plant, its ratio will become half as great in the atmosphere. This way the date of manufacture of any object made of wood or once living material can be ascertained.

Carbon dioxide, CO_2. Carbon dioxide is present in air to about 0.03-0.05 per cent (v/v) as a result of burning of carbon containing compounds such as wood, coal oil, wax, etc. It occurs in combined state in the carbonate minerals, e.g. limestone $CaCO_3$, dolomite $CaCO_3$. $MgCO_3$, etc.

It is prepared by burning carbon in the excess of air or by heating metal carbonates or bicarbonates with or without acids.

$$C+O_2 \longrightarrow CO_2$$

$$CaCO_3 \longrightarrow CaO+CO_2$$

$$CaCO_3+HCl \longrightarrow CaCl_2+H_2O+CO_2$$

(Lab. method)

$$2NaHCO_3 \longrightarrow Na_2CO_2+H_2O+CO_2$$

It can also be prepared by fermenation of glucose by yeast.

$$C_6H_{12}O_6 \longrightarrow 2C_2H_5OH+2CO_2$$

Carbon dioxide is a clourless gas with a faint pungent and slight acid taste. It is fairly soluble in water. It is liquefied at 293 K and 60 atmospheric pressure and solidfied. Solid carbon dioxide is called dry ice.

Carbon dioxide is used for extinguishing fire. It is also used in the manufacture of aerated water, white lead, baking soda, etc. A mixture of CO_2 and O_2 is used for artifical respiration.

Carbon dioxide cycle. Plants change carbon dioxide into sugar, starch, cellulose under the influence of sunlight and chlorophyll as described above. These materials are taken by animals as food. The plants on burning or decaying give carbon dioxide. Animals also exhale carbon dioxide. In this way carbon dioxide gas comes back in the atmosphere. Thus this is a never ending cycle in nature.

Carbon disulphide, CS_2 It is obtained by passing vapours of sulphur over red hot charcoal.

$$C+2S \longrightarrow CS_2 \qquad \Delta H—79.4\ kJ$$

It is a colourless liquid with characteristic smell. It is highly volatile (b.p. 319 K, m.p. 160 K). It is insoluble in water but solube in organic solvents. It is highly inflammable.

$$CS_2+3O_2 \longrightarrow CO_2+2SO_2$$

The mixture of carbon disulphide oxygen, air or nitric oxide is explosive.

$$2CS_2+5O_2 \longrightarrow 2CO+4SO_2$$
$$2CS_2+10NO \longrightarrow 2CO+4SO_2+5N_2$$

It reacts with slaked lime or sodium hydroxide to form corresponding thiocarbonate.

$$3Ca(OH)_2+3CS_2 \longrightarrow CaCO_3+2CaCS_2+3H_2O$$
$$6NaOH+3S_2 \longrightarrow Na_2CO_3+2Na_2CS_3+3H_2O$$

Its vapours are decomposed by hot metals.

$$CS_2+4K \longrightarrow 2K_2S+C$$

It reacts with phosphorus pentachloride to form thiocarbonyl chloride.

$$PCl_5+CS_2 \longrightarrow PSCl_3+CSCl_2$$

It is chiefly used as a solvent for sulphur, rubber, phosphorus, camphor, wax, fats, etc. It is also used in the manufacture of artificial silk and carbon tetrachloride. It is used as an insecticide. It is used for the extraction of oil from oilseeds.

Carborundum. Trademark for abrasives and refractories of silicon carbide, fused alumina, and other materials. Silicon carbide is produced by heating a mixture of sand and coal in a special electric furnace.

$$SiO_2+3C\rightarrow SiC+2CO$$

Covalent bonds between the Si and C atoms are responsible for an exceedingly high hardness of SiC. Carborundum is used in the manufacture of grinding wheels, coated abrasive products, and heating elements in furnaces.

Case-hardening. It is the process of giving a thin coating of hardened steel to a strong, flexible, mild steel by heating it in contact with charcoal and quenching in oil.

Central metallic ion. It is the metal ion that has sufficient number of empty orbitals which enable it to accept electron paris from ligands. Metal ions having small size and high nuclear charge from stable complexes. Among metals, the d-block or transition metals show the greatest and s-block (IA and II A) metals show the least tendency to from coordination compounds. All metallic ions in aqueous solution exist as coordination compounds in which the ligands are water molecules; e.g. Cu^{2+} in water really exists as $[Cu(H_2O)_4]^{2+}$

Cerium. [Named after the asteroid Ceres] Ce. A Group IIIA element of the 6th period of the Periodic Table of Elements, atomic number 58, atomic mass 140.12. Discovered in 1803 (two years after the asteroid) by Klaproth and, independently, Berzelius and Hisinger. The most abundant and extensively used lanthanide.

Properties A soft grey metal, reactive. The oxidation states in compounds +3 and +4.

Occurrence The chief ore is monazite.

Uses In the manufacture of special alloys possessing high ductility and resistance to heating, glasses that do not undergo darkening under radioactive irradiation, are electrodes, pyrophoric alloys, ignition devices. Cerium(IV) salts are strong oxidizing agents used in titrimetric determinations of various reducing agents.

Cesium [Latin *caesius*, bluish-grey] Cs. A Group IA element of the 6th period of the Periodic Table of Elements, atomic number 55, atomic mass 132.905. Contains one stable isotope, ^{133}Cs. Discovered by Bunzen and Kirchhoff in 1860 who observed its blue line in the spectrum of a mineral water sample.

Properties An alkali metal, very reactive, pyrophoric, decomposes water, reacts violently with other substances. The oxidation state in compounds +1.

Occurrence In the mineral lepidolite.

Manufacture As a by-product of lithium manufacture.

Uses Photocells.

Chain reaction. The process of nuclear fission usually emits two or three free neutrons per fission, besides the other fission. fragments. The fission, thus, is a peculiar type of nuclear reaction which has amongst its products the same kind of particles that initiated it. It is the emission of these neutrons which makes the process of nuclear fission a real source of energy. For example, when U-235 nucleus splits up, it generally release three neutrons; one of the neutrons may escape without hitting any other nucleus and gets lost. The other two may strike against other fissionable nuclei to produce further fission accompanied by the release of more neutrons and so on. Hence, if on an average, more than one neutron per fission product further fissions, the number of fissions which take place at each successive stage goes on increasing at an enormous rate giving rise to chain reaction.

Charcoal. There are several varieties of charcoal, each variety being named after the source from which it is obtained. For example, wood charcoal, sugar charcoal, animal charcoal, lamp black.

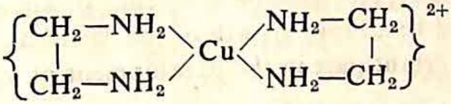
Wood charcoal is obtained by heating wood in the absence of air. It is used as a fuel, as a reducing agent and as a decolourising agent.

Sugar charcoal is obtained by heating sugar in the absence of air. It is the purest form of carbon.

Animal charcoal is left as a residue when bones are subjected to destructive distillation in a retort. It is used as an adsorbent and as a decolouriser.

Lamp black is prepared by burning tar and vegetable oils in the absence of air and depositing the soot on wet blankets. It is used for making printing ink and carbon paper.

Chelation. The capacity of a multidentate ligand to surroud a central ion by catching it at more than one points is called chelation and the complexes so formed are called chelates. For example, ethylenediamine forms chelate complex,



Generally chelates are more stable than coordination compounds containing only monodenate ligands.

Chelatomerty. A titrimetric technique exploiting the ability of some organic ligands to chelate the ions present in a solution at a sufficiently high rate. The most familiar example is the titration with ethylenediaminetetracetracetic acid and its analogues (aminopolycarboxylic acids) which react with most metal ions practically instantaneously to give stable water-soluble compounds of a constant composition. Amino polycarboxylic acids can be used for titrimetric determination of practically all cations and many anions.

Chemical bond. With the exception of noble gases, atom in general are in incapable of independent existence. Atoms of one element may combine with the atoms of the same element or of different elements and thus exist in the form of clusters of group or combination of atoms. These clusters of atoms are known as molecules. The force that holds the atoms together in a molecules is termed as the chemical bond.

Chemical reaction. A transformation of substances into other ones differing from the former in their compositions and properties; described by chemical equations. Unlike nuclear reactions chemical reactions do not cause transformations of atoms but only affect their states. There are several types of chemical reaction: combination, $2Cu+O_2 \rightarrow 2CuO$; decomposition, $2HgO \rightarrow 2Hg+O_2$; substitution, $Fe+CuSO_4 \rightarrow FeSO_4+Cu$; exchange, $NaCl+H_2SO_4 \rightarrow HCl+NaHSO_4$.

Chemistry. A science studying chemical elements and their compounds (their composition, properties, and structure), and interconversions of substances (chemical reactions). Chemistry is mainly divided into the inorganic, organic, physical, and analytical chemistry. Chemistry is intervolved with other sciences, and on its borders, such branches of study as biochemistry, geochemistry, etc. have been developed. The progress in chemistry has led to a rapid growth of the chemical industry which plays an important part in the development of all fields of industry.

Chloride. A compound of chlorine and a metal, a salt of hydrochloric acid.

Chlorinated lime (chloride of lime, bleaching powder). A mixture of calcium hypochlorite and calcium chloride, a white powder with a smell of chlorine. Made by the action of chlorine on dry slaked lime.

$$2Ca(OH)_2+2Cl_2 \rightarrow Ca(ClO)_2+CaCl_2+2H_2O$$

Used as an oxidizing agent, in the textile and paper industries, in the chemical industry, as a disinfectant.

Chlorination. The introduction of chlorine into molecules of inorganic and organic substances, widely used in the chemical industry.

Chlorine. Chlorine was discovered in 1774 by Scheele. He prepared it by heating hydrochloric acid (muriatic acid) with manganese dioxide and named it 'oxymuriatic gas' thinking it to be an oxide of the acid. It was Davy who established its elementary nature in 1800 and called it chlorine (Greek, *chloros* =greenish-yellow) because of its colour.

In the combined state chlorine is widely distributed as chlorides. Common salt (NaCl) is the most important chloride present in sea water and occurs as rock salt. Stassfurt deposits are composed largely of potassium and magnesium chlorides.

Chlorine can be prepared by the oxidation of hydrochloric acid.

At present it is manufactured by the electrolysis of brine solution.

Chlorine in used:

For bleaching woodpulp used for the manufacture of paper and rayon, and for bleaching cotton and linen textiles.

For purification of drinking water.

In organic chemical industry it is used for the manufacture of chloroform ($CHCl_3$); carbon tetrachloride (CCl_4) and ethylene chloride ($C_2H_4Cl_2$), solvents, refrigerants, DDT. synthetic plastics, rubbers, anti-knock compounds, etc.

In inorganic chemical industry it is used for the manufacture of bleaching powder, hypochlorites, chlorates perchlorates, bromine and hydrochloric acid (synthetic method).

For extraction of metals like gold and platinum.

In warfare for the manufacture of poisonous gases, e.g.

Phosgene, $COCl_2$; Tear gas, $CCl_3.NO_2$;
Mustard gas, $ClC_2H_4-S-C_2H_4Cl$.

Chlorine water. A solution of chlorine in water; the dissolution is accompanied by the reaction:

$$Cl_2+H_2O \rightleftharpoons HCl+HClO$$

Chlorine heptoxide, Cl_2O_7. tt is obtained by dehydrating perchloric acid with phosphorus pentoxide at 263 K. With water it forms perchloric acid. Thus it is perchloric anhydride.

$$2HClO_4 \underset{H_2O}{\overset{P_4O_{10}}{\rightleftharpoons}} Cl_2O_7$$

Cl_2O_7 is a colourless, oily liquid (bp. 355 K) which explodes on heating or striking. It is moderately stable.

Chlorine hexoxide, Cl_2O_6. It is prepared by the action of ozone over chlorine dioxide.

$$2ClO_2+2O_3 \dashrightarrow Cl_2O_6+2O_2$$

It is a red, explosive, oily liquid which dissociates on heating to its elements. It is a strong oxidizing agent and explodes in contact with grease. With alkalis it reacts to form chlorate and perchlorate.

$$C_2O_6+2OH^- \longrightarrow \underset{\text{chlorate}}{ClO_3^-}+\underset{\text{perchlorate}}{ClO_4^-}+H_2O$$

In liquid state it is diamagnetic but paramagnetic in gaseous state as ClO_3. Thus it may be regarded as a mixture of Cl_2O_6 and ClO_3.

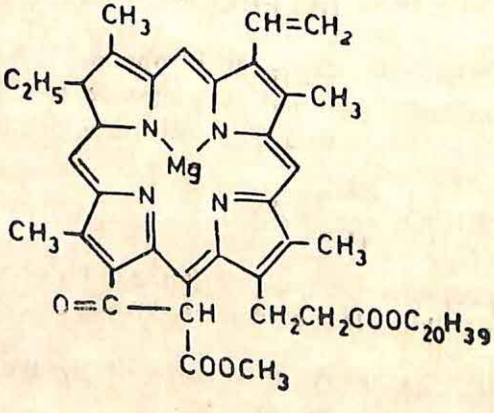
$$Cl_2O_6 \rightleftharpoons 2ClO_3$$

Chlorine trifluoride, ClF_3. It is prepared by heating chlorine with excess of fluorine in a copper vessel at 525 K.

$$Cl_2+3F_2 \longrightarrow 2ClF_3$$

It is a colourless gas. On condensation it gives a pale green liquid (b.p. 261 K), which crystallizes at 203 K to a white solid. It is very reactive compound and forms compounds with number of metals. It also reacts with glass. It is a good flourinating agent.

Chlorophyll. It is a magnesium containing pigment (structure given below). Green plants conduct the process of photosynthesis in the presence of sunlight and chlorophyll.



Chlorophyll

Chlorosulphonic acid, $HO.SO_2.Cl$. It is obtained by passing dry hydrogen chloride gas into oleum.

$$SO_3+HCl \longrightarrow HO.SO_3.Cl$$

It can also be obtained by the reaction of sulphuric acid on phosphorus pentachloride or phosphorus oxychloride.

$$H_2SO_4+PCl_5 \longrightarrow HO.SO_2.Cl+POCl_3+HCl$$
$$2H_2SO_4+POCl_3 \longrightarrow 2OH.SO_2.Cl+HPO_3+HCl$$

Chromate. A metal salt of chromic acid, H_2CrO_4. Made by the oxidation of chromium(III).

$$2KCrO_2+3H_2O_2+2KOH \rightarrow 2K_2CrO_4+4H_2O$$

The reaction is accompanied by a change in solution colouration from green to yellow characteristic of the CrO_4^{2-} ion. In acid solutions the chromate ion is transformed into the dichromate ion having an orange colour:

$$2CrO_4^{2-}+2H^+ \rightleftharpoons 2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-}+H_2O$$

Metal chromates are used as strong oxidizing agents and as pigments. Lead chromate, $PbCrO_4$ is a bright-yellow compound, slightly soluble in water; used as a yellow oil-colour pigment (chrome yellow).

Chromatography. A method for separating and analysing mixtures of substances based on differences in sorption of the mixture components by a given sorbent. First suggested (1903) by Tswett. The separation is carried out in columns filled with silica gel, alumina, ion exchangers, etc. or on special paper. Because of different sorption of mixture components (the mobile phase) they are separated into zones along the column packed with a sorbent (the stationary phase) to produce a chromatogram which can be used to isolate and analyse individual substances (the process is analogous to many-step rectification). Depending on the state of aggregation of the sample (mobile phase) chromatography may be gas and liquid; depending on the separation mechanism the chromatographing techniques are classified as ion exchanging, precipitation, partition, and molecular (adsorption). Lastly, chromatography can be carried out on columns (column chromatography), special porous paper (paper chromatography), in capillaries (capillary chromatography), and thin sorbent layers (thin layer chromatography). Chromatography is applied to analyse mixtures of inorganic and organic substances, to concentrate traces of elements. In the chemical industry, it is used in the purification and separation of substances. It provides a means for analysing mixtures of substances having related properties (e.g. lanthanides, actinides, isotope mixtures, mixtures of amino acids, hydrocarbons).

Chromel. Tradename for a series of nickel-chromium alloys; used, e.g. in pyrometry as a material for thermocouples.

Chrome plating. A coating of metals and various articles with chromium to prevent corrosion.

Chromic acid mixture. A solution of potassium or sodium dichromate in concentrated H_2SO_4. A strong oxidizing agent. Used to oxidize organic substances, to wash laboratory ware.

Chrome alum, $K_2SO_4.Cr_2(SO_4)_3.24H_2O$. Chromic sulphate gives double salts with sulphates of alkali metals and the double salts are called alums, e.g. with potassium sulphate it gives chrome alum.

In the laboratory chrome alum is prepared by reduction of an acidified solution of potassium dichromate with sulphur dioxide.

$$\begin{array}{c} K_2Cr_2O_7+4H_2SO_4 \rightarrow K_2SO_4+Cr_2(SO_4)_3+4H_2O+3(O) \\ SO_2+H_2O+O \rightarrow H_2SO_4 \times 3 \\ \hline K_2Cr_2O_7+H_2SO_4+3SO_2 \rightarrow K_2SO+Cr_2(SO_4)_3+H_2O \end{array}$$

Beautiful deep violet octahedral crystals of chrome alum separate on standing. These dissolve in water giving violet solution which changes green when heated to 365 K.

Chrome alum is obtained in large quantities as a by-product in the manufacture of anthraquinone, from anthracene.

Chrome alum is used in dyeing as a mordant, in leather industry for tanning (preparation of chrome leather—chrome-tanning), and in photography (during fixing) for hardening of negatives.

Ammonium chrome alum may be similarly prepared by using ammonium dichromate. This alum is also used for tanning and in calico-printing.

Chromium. L.N. Vauquelin, a French chemist, discovered a new element in 1797 while examining a mineral found in Siberia. It was named chromium because it formed coloured compounds (Greek word, *chroma* means colour).

Chromium does not occur free in nature. Its principal ore is chromite or chrome iron ore, $FeO.Cr_2O_3$. It is also found as chrome ochre, Cr_2O_3 and crocoisite, $PbCrO_4$. Chrome iron-ore is found in large quantities in South Africa, Turkey, Russia and India. In India the chromite ores occur in Karnataka, Bihar and Orissa, near Salem in Tamil Nadu and in the Andaman Islands.

Ferrochrome, an alloy of chromium and iron, is prepared by the reduction of chromite with carbon in an electric furnace. It contains 60-70 per cent chromium and 1-8 per cent carbon. It is largely used in the manufacture of chrome-steel.

$$Fe.OCr_2O_3+4C\rightarrow Fe+2Cr+4CO$$

Pure metallic chromium is obtained by the reduction of chromic oxide free from iron which is prepared from the chromite ore.

Chromium in used in chrome plating, in the manufacture of alloy steel and other alloys like nichrome and stellite.

Chromium(III) oxide, Cr_2O_3. It is prepared by heating ammonium dichromate or a mixture of ammonium chloride and potassium dichromate.

$$2NH_4Cl+K_2Cr_2O_7\longrightarrow Cr_2O_3+N_2+4H_2O+2KCl$$

$$(NH_4)_2Cr_2O_7\longrightarrow Cr_2O_3+N_2+4H_2O$$

It can also be prepared by heating sodium dichromate with sulphur.

$$Na_2Cr_2O_7+S\longrightarrow Na_2SO_4+Cr_2O_3$$

It is obtained by heating $Cr(OH)_3$.

$$Cr(OH)_3\longrightarrow Cr_2O_3+3H_2O$$

it is a highly stable green powder.

It is amphoteric in nature. Thus it dissolves easily in acid as well as bases.

$$Cr_2O_3 + 6H^+ + 3H_2O \longrightarrow 2[Cr(H_2O)_6]^{3+}$$
$$Cr_2O_3 + 2OH^- + 3H_2O \longrightarrow 2[Cr(OH)_4]^-$$

When fused with alkalis, it forms chromates.

$$2Cr_2O_3 + 8KOH + 3O_2 \longrightarrow 4K_2CrO_4 + 4H_2O$$

Because of its low solubility in water and its bright green colour, it is used as a pigment under the name of chrome green.

Chromyl chloride, CrO_2Cl_2. It is a chromium(VI) compound. It is prepared by distilling a mixture of potassium dichromate, sodium chloride and concentrated H_2SO_4.

$$\begin{array}{rl} K_2Cr_2O_7 + 2H_2SO_4 \longrightarrow 2KHSO_4 + 2CrO_3 + H_2O & \\ NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl &] \times 4 \\ CrO_3 + 2HCl \longrightarrow CrO_2Cl_2 + H_2O &] \times 2 \\ \hline K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \longrightarrow 2KHSO_4 + 4NaHSO_4 & \\ + 3H_2O + 2CrO_2Cl_2 & \end{array}$$

The above reaction can also be represented by the ionic equation,

$$Cr_2O_7^{2-} + 4Cl^- + 6H_2SO_4 \longrightarrow 2CrO_2Cl_2 + 3H_2O$$

It can also be prepared bo the action of gaseous hydrogen chloride on chromic anhydride.

$$CrO_3 + 2HCl \longrightarrow CrO_2Cl_2 + H_2O$$

It is a deep-red liquid which boils at 490 K.

It reacts violently with water, giving chromic acid and hydrochloric acid.

$$CrO_2Cl_2 + 2H_2O \longrightarrow H_2CrO_4 + HCl$$

It is soluble in CS_2 and nitrobenzene.

When vapours of CrO_2Cl_2 are passed into concentrated solution of a chloride, a chlorochromate is formed.

$$CrO_2Cl_2 + NaCl + H_2O \longrightarrow \underset{\text{sodium chlorochromate}}{NaCrO_2Cl} + 2HCl$$

It is a powerful oxidizing agent and oxidizes toluene to benzaldehyde (Etard's reaction).

$$C_6H_5CH_3 \xrightarrow{CrO_2Cl_2} C_6H_5CHO+H_2O$$

Chromyl chloride test is used for the detection of chloride radical.

Chromyl chloride test. When potassium dichromate is heated with conc. H_2SO_4 and a soluble chloride such as sodium chloride, red vapours of chromyl chloride are obtained.

$$\begin{array}{c} K_2Cr_2O_7+\rightarrow 2H_2SO_4\rightarrow 2KHSO_4+2CrO_3+H_2O \\ [NaCl+H_2SO_4\rightarrow NaHSO_4+HCl]\times 4 \\ [CrO_3+2HCl\rightarrow CrO_2Cl_2+H_2O]\times 2 \\ \hline K_2Cr_2O_7+4NaCl+6H_2SO_4\rightarrow 2KHSO_4+4NaHSO_4+2CrO_2Cl_2 \\ +3H_2O \end{array}$$

When vapours of chromyl chloride are passed through sodium hydroxide solution, sodium chromate is produced. The solution is acidified with acetic acid and lead acetate added when yellow ppt. of lead chromate is obtained.

$$CrO_2Cl_2+4NaOH\rightarrow Na_2CrO_4+2NaCl+2H_2O$$

$$Na_2CrO_4+(CH_3COH)_2Pb\rightarrow \underset{\text{(yellow ppt.)}}{PbCrO_4}+2CH_3COONa$$

Clathrate. A clathrate is a "compound" in which atoms or molecules are trapped in holes in the crystal lattice of another substance. Argon, krypton, and xenon have been observed to form clathrates in certain organic solids and in ice.

Coal. A general term for solid fuels of the plant origin such as peat, lignite, bituminous coal, anthracite.

Coal tar. A viscous blak liquid with a characteristic phenol odour, formed in coking of coal. Coal tar is a complex mixture where aromatic substances such as benzene, toluene, xylene, naphthalene, anthracene, and phenol predominate; used as a raw material for their manufacture. Also used in building, paving, and as a fuel.

Cobalt [Greek *kobold*, a demon of the mines]. A Group VIII element of the 4th period of the the Periodic Table of Elements, atomic nuber 27, atomic mass 58.9332. Natural cobalt contains one stable isotope,^{59} Co. Discovered by Brandt in 1735.

Properties A solid with a metallic glitter and blue cast, ductile and malleable. Compact metal is not oxidized in the air; at 675 K, a thin coating of cobalt oxide is formed on its surface. Slowly dissolves in dilute HCl, H_2SO_4, and HNO_3. The oxidation states in compounds +2, +3. Halogens react with cobalt even at room temperature. Forms basic oxides of the compositions CoO, Co_2O_3, and Co_3O_4. Cobalt forms various complex ions, e.g. $[Co(NH_3)_6]^{3+}$, $[Co(NH_3)_5H_2O]^{3+}$, $[Co(NO_2)_6]^{3-}$, and numerous coordination compounds.

Occurrence A scattered element, found in many igneous rocks, sea water, mineral springs. Cobalt minerals are known (e.g. cobaltite). Found in soil, in plants and animals, occurs as admixtures in ores of copper, nickel, and some other metals.

Uses In the manufacture of various special alloys and steels, as a catalyst, in agriculture (a microfertilizer). The ^{60}Co radioactive istope is widely used as a source of gamma-radiation in the radiation chemistry, medicine, radiography, for thickness and density measurements. Cobalt is essential to man, Cobalt compounds are used in the manufacture of pigments and enamels.

Coefficient of variation. It is given by the expression:

$$\text{C.V.} = \frac{\text{Standard deviation} \times 100}{\text{Mean}}$$

(where C.V. is coefficient of variation).

Colloidal platinum. A colloidal sulution of platinum can be prepared by Bredig's method.

Spongy platinum, platinum black and platinized asbestos absorb large quantities of oxygen gas (100-110 times their volume) and then act as oxidizing agents.

Complex. A complex is a chemical combination in which a central atom (usually a metal) or ion is surrounded by a number of other molecules or ions which are already formed in a normal way.

A complex has different properties from the constituents of which it is made up of. For example, when a ferrous cyanide solution is mixed with potassium cyanide, potassium ferrocyanide is formed which in aqueous solution does not give tests for Fe^{2+} and CN^- ions but gives the test of $[Fe(CN_6)]^{4-}$.

$$K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$$

Thus $K_4[Fe(CN)_6]$ is a complex whereas $[Fe(CN)_6]^{4-}$ is a complex ion.

Conduction electrons. In a typical metal the valence electrons are no longer bound to specific atoms, but are free to move throughout the solid. These electrons are responsible for the high electrical and thermal conductivity of metallic solids, and consequently are called conduction electrons.

Confidence limits (or confidence interval). It is given by the expression:

$$\text{Confidence limit} = \bar{x} \pm \frac{ts}{\sqrt{N}}$$

(where t is a statistical factor that depends on the number of degrees of freedom, N and the confidence limit; s is the estimated standard deviation).

Converter. A furnace for the manufacture of steel from molten pig iron by blasting air or air enriched in oxygen through the melt.

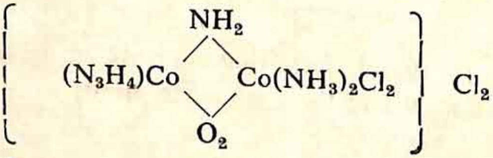
Coordination compound. (Werner complex). A compound or a complex ion formed by the addition of neutral molecules or ions called ligands to a given ion or atom (the central ion). Unlike double salts coordination compounds dissociate in solutions only slightly; can contain a complex anion, e.g. $[Fe(CN)_6]^{3-}$ a complex cation, e.g. $[Ag(NH_3)_2]^+$, or give no ions at all upon dissolution (nonelectrolytetype compounds). Coordination compounds are numerous and varied. They are used in chemical analyses, in industry for the recovery of some metals from their ores (gold, silver, platinum family metals, etc.), for separating mixtures of elements (e.g. mixtures of lanthanides). They play an important role in plant and animal life; e.g. chlorophyll and haemoglobin are coordination compounds.

Coordination isomerism. This type of a isomerism arises when both the cation and the anion of coordination compound are complexes and there occurs a redistribution of the ligands between the two coordination spheres. For example:

$[Co(NH_3)_6]^{2+}[Cr(CN)_6]^{3-}$ and $Cr(NH_3)_6]^{3+}[Co(CN)_6]^{3-}$
$[Co(NH_3)_6{}^{3+}[Cr(ox)_3]^{3-}$ and $[Cr(NH_3)_6]^{3+}[Co(ox)_3]^{3-}$
$[Cu(NH_3)_4]^{2+}[PtCl_4]^{2-}$ and $[Pt(NH_3)_4]^{2+}[CuCl_4]^{2-}$

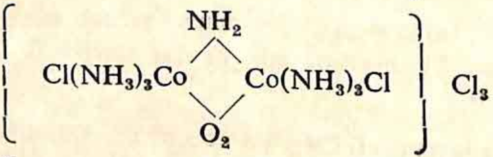
Coordination number. The maximum number of ligands (neutral molecules or negative ions) which can be coordinated to a central metal atom or ion is known as the coordination number of a central atom or ion in a particular combination. In $K_3[Fe(CN)_6]$, six cyanide ligands are coordinated to Fe^{3+} and hence coordination number of Fe^{3+} is six.

Coordination position isomerism. This type of isomerism arises in polynuclear complexes by an interchange of ligands between the different metal atoms. For example:

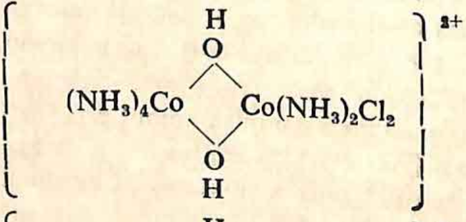


$$\left[(N_3H_4)Co\underset{O_2}{\overset{NH_2}{\diamond}}Co(NH_3)_2Cl_2\right]Cl_2$$

and

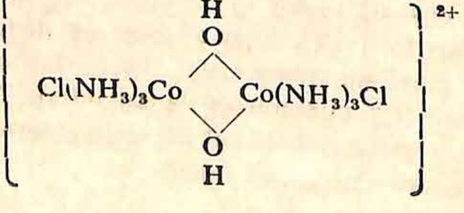


$$\left[Cl(NH_3)_3Co\underset{O_2}{\overset{NH_2}{\diamond}}Co(NH_3)_3Cl\right]Cl_3$$



$$\left[(NH_3)_4Co\underset{\underset{H}{O}}{\overset{\overset{H}{O}}{\diamond}}Co(NH_3)_2Cl_2\right]^{2+}$$

and



$$\left[Cl(NH_3)_3Co\underset{\underset{H}{O}}{\overset{\overset{H}{O}}{\diamond}}Co(NH_3)_3Cl\right]^{2+}$$

Coordination theory. The theory of coordination compounds suggested by Werner in 1893. According to that theory, one of the ions (usually a positively charged ion) occupies the central position in any coordination compound (the central ion). In its nearest envirnment, a number of ions of the opposite charge or neutral molecules called ligands (addends) are arranged: these form the internal coordination layer (sphere). Other ions are farther from the central ion and form the outer coordination layer (sphere). Thus in $K_2[PtCl_6]$, the platinum ion is the central ion, the chloride ions are the ligands, and potassium occurs in the outer sphere.

Copper. Copper occurs in nature even as a pure metal. This accounts for about 6% of the used deposits. Cosmically, copper is relatively abundant as compared to other heavy metals; 100-400 ppm are found in the metal phase of meteoric iron. The high affinity of copper for sulphur is the major factor in determining the manner of occurrence in the earth's crust. Copper is obtained from the ores by smelting, leaching or electrolysis.

In sea water, most reports have indicated concentrations from 1-5 μg/L. In American rivers concentrations ranging from 0.83 to 105 μg/L have been reported. In drinking water very large variations in concentrations from a few μg to more that 1 mg/L have been reported.

Natural copper concentrations in soil vary from 2 to 100 mg/kg dry weight. Air levels of copper in the US have been reported to vary from 10-570 ng/m^3; the highest values being found in urban areas. At the south pole the average copper concentration in air is 0.036 ng/m^3.

The daily intake of copper from blood generally varies from about 1 to about 3 mg, corresponding to about 15-45 μg/kg by wt. in adults. Cereals contain less copper and milk is relatively poor in copper. Concentrations in food are generally around 1 mg/kg. Copper-poor items such as milk usually contain less than 0.1 mg/kg. The normal concentrations of copper in whole blood, plasma and erythrocytes have been reported to be around 1 mg/L. Data from children of different age groups indicate that about 1 μg/kg by wt. is excreted daily via the urine upto the age of 12. In adults daily excretion has been found to be less than 100 μg/day, usually around 20 μg/day.

The primary use of copper, accounting for approximately half of the production, is in electrical equipment. Copper has a very high electrical conductivity per unit volume. It can be drawn readily into wires, either single or multifilment. Copper is also a component of many alloys where it may occur together with other metals, such as silver, cadmium, tin and zinc. It was used for tools, ornaments, pots for cooking and coinage. Low corrosion rates coupled with ease of forming, bending and of copper tubing resulted in extensive uses of copper for domestic water pipe. Other important uses are in plumbling, and heating copper salts may serve as pesticidies.

Reliable methods for determination of copper in biological material have been available for many decades. The most common colorimetric method allows sodium diethyldithiocarbamate to form a yellow complex with copper, which can be extracted into an organic solvent, usually amyl alchohol. Blood and urine values obtained with this method agree well with recently published results obtained with more modern teceniques.

Emission spectroscopy, neutron activation, atomic absorption spectrophotometry and electrochemical methods, e.g. pulse polarography, anodic stripping voltametry, have all been used for the determination of copper in biological and environmental samples. Concentrations of 0.01-0.1 mg/kg can easily be determined by such methods. Atomic absorption spectrophotometry, the most common method at present, may detect a few ng of copper, especially with flameless atomization making it possible to use microliter volume of blood and plasma.

There are no interlaboratory comparisons of different methods available, but the good agreement between results obtained in, for example, blood and urine in different areas of the world during many decades suggests that copper can be accurately determined by several methods in most materials.

Though emission spectoscopy and AAS methods are very convenient from the analyst's point of view but the accessibility of these instrumental facilities to a common analyst/chemist becomes a hurdle in the choice and one looks for some alternate instrument and method. Spectrophotometric methods then become the methods of choice; those employing dithizone and sodium diethyl-dithiocarbamate to develop yellow-brown colours absorbing at 550 nm and 436 nm respectively are quite popular.

Diphenylcarbazide, is a well-known reagent for the determination of copper. A related reagent, diphenylcarbazone, is also adopted.

Several sensitive methods for the determination of copper are based on azo reagents, such as PAN, 2-(5-nitro-2-pyridylazo)-1-naphthol, 2-(2-pyridylazo)-1-naphthol (O-α-PAN), PAR, 2-(2-thiazolylazo)-5-dimethylaminophenol (TAM), 1-(2-thiazolylazo)-2-naphthol (TAN), Picramine R, Picramineepsilon, Aminomethylazo III, other bisazo derivatives of chromotropic acid, Acid Alizarin Black SN, Zincon, Calcichrome, Azo-azoxy BN and Magneson Khs.

Many methods are based on oximes, e.g. α-furildioxime, α-benzoinoxime (cupron), Salicylaldoxime, acetylacetonedioxime, pyridine-2, 6-diacetoxime, methyl-2-pyridylketoxime. The coloured copper complexes formed with most of these reagents can be extracted into chloroform of isoamyl alcohol.

Copper sulphate. Copper sulphate ($CuSO_4.5H_2O$), krown as blue vitriol, is an important compound of copper. It is obtained by treating scarp copper with hot dil. H_2SO_4 in presence of air.

$$2Cu+2H_2SO_4+O_2 \longrightarrow 2CuSO_4+2H_2O$$

Blue crystalline copper sulphate is soluble in water. Its aqueous solution is acidic because of the following reaction:

$$CuSO_4+2H_2O \longrightarrow \underset{\substack{\text{(weak}\\ \text{base)}}}{Cu(OH)_2}+\underset{\substack{\text{(strong}\\ \text{acid)}}}{H_2SO_4}$$

Corrosion of metals. Latin corrodere, to gnaw to pieces. The destruction of metals under the action of medium with the oxidation of metal atoms to metal ions; rusting of iron is an example.

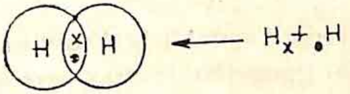
$$4Fe + 2H_2O + 3O_2 \rightarrow 2(Fe_2O_3.H_2O)$$

To prevent corrosion, metal surfaces are coated with oil colours, lacquers, enamels, or thin layers of other metals. An oxide film is formed on the surface of aluminium metal brought in contact with air oxygen: the film protects the metal from further corrosion. The rate of corrosion is especially high if two dissimilar metals such as iron and zinc or iron and tin touch each other and thus form a galvanic cell (electrochemical corrosion).

Corundum. Al_2O_3. Natural aluminium oxide with minor admixtures of other elements determinining its colouration. The purest transparent varieties are red ruby and blue sapphire. Corundum mixed with other minerals is called emery. Corundum is chemically stable, insoluble in acids, the hardest substance after diamond. Used as an abrasive. Corundum crystals can be grown artificially from aluminium oxide.

Cosmic rays. A primary cosmic ray is an ultra-high-energy particle which, trapped by the earth's magnetic field, comes barreling into the earth from outer space. These particles include protons; when they collide with atmospheric molecules, secondary cosmic rays result. These are also very energetic and are responsible for most of the genetic and somatic damage done to living tissue.

Covalent bond. A bond formed by the mutual sharing of a pair of electrons between two atoms, each atom contributing one electron, is called the covalent bond. The shared pair of electrons will not belong to any one particular atom but will belong to both the atoms simultaneously. For example, a hydrogen molecule consists of two atoms of hydrogen, each having one electron in its valence shell ($1s^1$). Each hydrogen atoms contributes one electron towards a pair shared by the two atoms:



Covalent carbides. The carbides of boron and silicon (B_4C and SiC) are truly covalent carbides. These are chemically inert, thermally stable and hard solids. The carbides such as CH_4, CCl_4, CS_2, etc. are not included in covalent carbides even there is covalent bond between the atoms. These are eithnr gases or volatile liquids and thermally unstable. These are infact, classified as hydride chloride, sulphide, etc. of carbon respectively.

Covalent halides. Halides of non-metals such as PCl_3, $SiCl_4$, IF_3 are essentially covalent. These are generally volatile liquids which are non-conductors of electricity and undergo hydrolysis when treated with water to form the halogen acid and the oxy-acid of the less electronegative element which corresponds to the oxidation states of this element in the halide. For example,

PCl_3	$+3H_2O \rightarrow$	H_3PO_3	$+3HCl$
(oxidation state of $P=+3$)		(oxidation state of $P=+3$)	
$SiCl_4$	$+3H_2O \rightarrow$	H_2SiO_3	$+4HCl$
(oxidation state of $Si=+4$)		(oxidation state of $Si=+4$)	

Halides of the first row non-metals, e.g. CF_4, CCl_4 and NF_3, are resistant to hydrolysis. This is because in a covalent halide hydrolysis occurs as a result of co-ordination of a water molecule to the less electronegative element which is not possible in the first row elements as they cannot expand their octets.

Covalent halides are conveniently prepared by direct combination of the constituent elements.

$$P_4 + 6Br_2 \rightarrow 4PBr_3$$

Some of the chlorides are prepared by passing dry chlorine over a heated mixture of the non-metal oxide and carbon.

$$SiO_2+2C+2Cl_2 \rightarrow SiCl_4+2CO$$

Crystal-field theory. Crystal-field theory was originally developed to account for properties (energy levels, bond energies, symmetry, etc.) of ions in ionic crystals. Its focus is the calculation of the electric field witihin a crystal. It forms the basis for the broader, more sophisticated ligand-field theory.

Crystal or metallic radius. The radius derived from the crystalline structure of a metal is referred to the crystalline or metallic radius. One-half of the distance between the nuclei of two adjacent atoms in the metallic crystal gives the metallic or crystalline radius. Since metal atoms are bound by unique metallic bond forces in the solid, the metallic or crystal radius is quite different from other types of radius, viz. covalent, ionic or van der Waals radius.

Cuprous chloride, CuCl. It is obtained by heating cupric oxide or cupric chloride or copper sulphate with excess of copper turnings and conc. hydrochloric acid.

$$CuO+Cu+2HCl \longrightarrow 2CuCl+HO_2$$
$$CuCl_2+Cu \longrightarrow 2CuCl$$
$$CuSO_4+Cu+2HCl \longrightarrow 2CuCl+H_2SO_4$$

Cuprous chloride forms a soluble complex $H[CuCl_3]$ with concentrated HCl but separates out as milky white crystalline precipitate when the solution is poured in water.

It may also be prepared by heating metallic copper with excess of conc. HCl in presence of a little $KClO_3$ or HNO_3 (which supplies oxygen).

$$Cu+2HCl+O \longrightarrow CuCl_2+H_2O$$
$$CuCl_2+Cu \longrightarrow 2CuCl$$

The reaction mixture is poured in water when cuprous chloride is precipitated.

It is also prepared by passing SO_2 through a solution of $CuSO_4$ containing NaCl when CuCl is precipitated.

$$Cu^{2+}+e^- \longrightarrow Cu^+]\times 2$$

$$SO_2+2H_2O \longrightarrow SO_4^{2-}+4H+2e^-$$

$$\overline{2Cu^{2+}+SO_2+2H_2O \longrightarrow 2Cu^+ + SO_4^{2-}+4H^+}$$

$$\Big\downarrow +Cl^-$$

$$CuCl$$

It is also formed when $CuCl_2$ is strongly heated (725 K).

$$2CuCl_2 \longrightarrow Cu_2Cl_2+Cl_2$$

It is a white solid almost insoluble in water but soluble in conc. HCl with which it gives the complex ions.

$$CuCl+3Cl^- \rightleftharpoons [CuCl_4]^{3-}$$

It dissolves in aqueous ammonia forming a colourless solution due to the formation of the complex $Cu(NH_3)_4Cl$. This solution absorbs carbon monoxide forming $CuCl.CO.2H_2O$.

It also reacts with acceylene to give a red precipitate of cuprous acetylide.

In air, it is slowly oxidized to green basic cupric chloride,

$$3CuO.CuCl_2.3H_2O$$

When treated with oxidizing agents, it is coverted into cupric chloride.

$$2CuCl+2HCl+(O) \longrightarrow 2CuCl_2+H_2O$$

Curprous chloride reacts with NaOH forming a yellow precipitate of cuprous oxide which turns red on boiling.

$$2CuCl+2NaOH \longrightarrow Cu_2O+2NaCl+H_2O$$

Hydrogen sulphide reacts with CuCl to give a black precipitate of cuprous sulphide.

$$2CuCl+H_2S \longrightarrow Cu_2S+2HCl$$

Cuprous chloride is used in the gas analysis for absorbing carbon monoxide and acetylene (ammoniacal for absorbing acetylene and HCl solution for absorbing CO and oxygen).

Cuprite. A red ore of copper, Cu_2O, contains 88.8 per cent copper.

Curie. A measure of the activity of a radioactive substance; one curie correspondes to 3.7×10^{10} disintegrations per second. Named after Marie Curie. Derivative units: 1 millicurie$=10^{-3}$ curie, 1 microcurie$=10^{-6}$ curie.

Curium. (At. No. 96). The fourth transuranium element was discovered as a by-product obtained by bombarding plutonium-239 with alpha particles from the Berkeley cyclotron. It was named Curium in honour of Marie and Pierre Curie. The nuclear reaction is as under:

$$^{239}_{94}Pu + ^{4}_{2}He \longrightarrow ^{242}_{96}Cm + ^{1}_{0}n \text{ (half-life of 162 days)}$$

The very short life of this alpha-emitting isotope makes it extremely hazardous for investigation.

Cyanide. A salt of hydrocyanic acid, e.g. potassium cyanide KCN, sodium cyanide, NaCN. Used in the extraction of gold and silver from their ores (one of the methods of hydrometallurgy: the metals dissolve in cyanide [solutions because of the formation of complex salts), in electroplating (gilding), in the organic synthesis, sometimes for nitriding steel, etc. Cyanides are used in the analytical chemistry for separating metals. Highly poisonous.

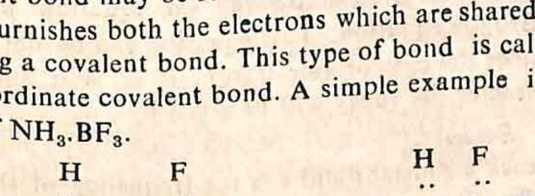
Cyanogen. $(CN)_2$ A colourless poisonous gas with a pungent odour; an analogue of halogens in some of its chemical properties.

D

Data analysis. (Measurement in chemistry). The primary basis of chemistry—like that of all the other sciences—is the information obtained through experiments. An experiment involves observation of a phenomenon (e.g. melting of a substance, growth of a crystal, reaction between substances) under controlled conditions. The quantitative aspects of a phenomenon (e.g. the temperature at which a substance melts, the rate at which a crystal grows, the amount of energy released/absorbed during a reaction) involve measurement of one or more quantities. All of us are familiar with the mearurement of distances, heights, weights, temperatures, etc. in daily life. In chemical science, one needs to measure not only these variables but many more like pressure, volume, concentration, density, etc. Let us now consider the process of measurement and the manner in which the result of a measurement is expressed.

Every measurement compares a physical quantity to be measured with some fixed standard, known as the unit of measurement. For example, when we say that the width of a page is 8.63 centimetres (usually written as 8.63 cm), we mean that the width is 8.63 times the unit of measurement, which is one centimetre in this case. The width of the page is obtained by using a scale with centimetre and millimetre markings. To express the result of a measurement, two pieces of information are required—the number (8.63) and the unit (centimetre). The measurement of any quantity in science is based on the same procedure.

Dative bond. We know that both water and ammonia can combine with Cu(II) ion and form blue and deep blue coloured ions $[Cu(H_2O)_4]^{2+}$ and $[Cu\ (NH_3)_4]^{2+}$. Interestingly neither water nor ammonia molecule has any unpaired electron which could share with the unpaired electron in Cu^{2+} ion and form a covalent bond. J.N. Lewis suggested that in such cases a covalent bond may be formed between two atoms, of which one atom furnishes both the electrons which are shared by the atoms forming a covalent bond. This type of bond is called the dative or co-ordinate covalent bond. A simple example is the formation of $NH_3.BF_3$.



$$\mathrm{H:\overset{\overset{H}{\cdot\cdot}}{\underset{\underset{H}{\cdot\cdot}}{N}}:} + \mathrm{\overset{\overset{F}{\cdot\cdot}}{\underset{\underset{F}{\cdot\cdot}}{B}}:F} \longrightarrow \mathrm{H:\overset{\overset{H}{\cdot\cdot}}{\underset{\underset{H}{\cdot\cdot}}{N}}:\overset{\overset{F}{\cdot\cdot}}{\underset{\underset{F}{\cdot\cdot}}{B}}:F}$$

d-Block elements. The elements which have party filled d sub shell in their elementary form or in their chemically significant oxidation states are called d block elements. In these elements the penultimate shell is being expanded from 8 to 18 electrons by the addition of ten d electrons.

There are three series of d block elements each containing ten elements.

First Series. Also called 3d series)—From scandium (Sc) to zinc (Zn).

Second Series. (Also called 4 d series)—From yttrium (Y) to cadmium (Cd).

Third Series. (Also called 5d series)—From lanthanum (La) to mercury (Hg).

As can be seen from the table, on p. 85 the elements Zn, Cd and Hg do not have a party filled d sub-shell either in the elementary form or in their chemically significant+2 oxidation state Therefore, these elements do not show much resemblance in properties with those of d block elements. However, they are generally studied with the d block elements, because of the similarities of these elements (such as complex formation) with other d block elements.

In the periodic table, on the left-hand side s block elements are present while on the right-hand side p-block elements are present. In between the two, there are d block elements. These are also called transition elements because they can be regarded as effecting a transition from the electropositive elements (s-block) to the electronegative elements (p-block).

de Broglie wave equation. Considering the wave-particle duality in matter, de Broglie derived an equation which is known as de Broglie equation. This equation can be derived as follows Consider the case of an electron. If it is assumed to have wave character, its enegy will be given by

$$E=h\nu$$

where h is Planck's constant and ν is the frequency of the electron wave. On the other hand if the electron is supposed to have particle nature its energy can be given according to Einstein's equation, as

d-Block Elements

3d series	Sc $3d^1, 4s^2$	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn $3d^{10}, 4s^2$
4d series	Y $3d^1, 5s^2$	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd $4d^{10}, 5s^2$
5d series	La $5d^1, 6s^2$	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg $5d^{01}, 6s^2$

$$E=mc^2$$

Also it is known that

$$c=\lambda\nu$$

or $$\nu=\frac{c}{\lambda}$$

Hence, $$h\frac{c}{\lambda}=mc^2$$

or $$\lambda=\frac{h}{mc}$$

λ is called de Broglie's wavelength and the equation is called de Broglie's wave equation.

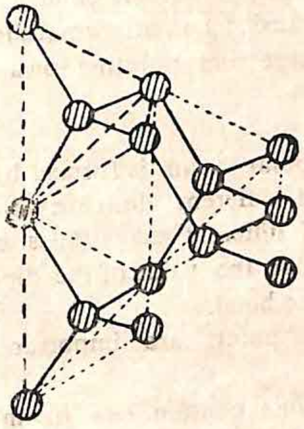
Detergent. Originally the word detergent referred to any good cleaning agent. The first detergents were the soaps, whose long anions have a hydrophilic end (which tends to dissolve in water) and a hydrophobic end (which tends to dissolve in oils, fats, and greases). When the alkylbenzene sulphonates (ABS) became popular because they do not precipitate ions such as calcium ions from hard water the term ''detergent'' was commonly used to refer to these ABS molecules. Now that the linear alkylbenzene sulphonates (LAS) are in common use, the word "detergent" generally refers to the whole mixture of ingredients (LAS, builder, etc.) which has been formulated and sold commercially. The term is generally no longer applied to soaps.

Determinate crrors. These are erros which are determinable. They may be classified as:

Instrumental errors,
Operative errors, and
Methodic crrors.

Diamagnetism. Diamagnetism is a weak repulsion from a magnetic field (away from a megnet). Since electrons are responsible for diamagnetism, and since all substances contain electrons, all substance are to some extent diamagnetic. Many, however, are also paramagne tic or ferromagnetic, and these effects are so powerful they obscure the normally weak diamagnetism. Bismuth shows an unusually high diamagnetism, which can be observed readily by suspending a piece of bismuth from the ceiling and observing its repulsion hy a powerful magnet.

Dimond. It is the purest from of carbon. It is the hardest substance known. Each carbon atom of diamond is attached to four other carbon atoms through four strong covalent bonds. This structure makes diamond the hardest natural substance known.



Structure of diamond.

It is the hardest known substance.
It is bad conductor of heat and electricity.
It has high refractive index (2.5).
Its specific gravity is 3.5.
On very strong heating in air it is converted to CO_2, leaving no ash.
It is used as gem in jewellery.
Black diamonds are used for cutting glass and drilling rocks.

Dipole moment. A polar molecule like HF having two centres of charge is called a dipole. The degree of polarity in a polar compound is specified by its dipole moment (μ), which is equal to the charge times the distances between the positive and negative centres. Mathematically,

$$\underset{\text{(in Debye units D)}}{\text{Dipole moment)}\ \mu} = \underset{\substack{\text{electronic}\\ \text{charge in}\\ \text{esu}}}{e} \times \underset{\substack{\text{distance}\\ \text{in Angstrom}}}{d}$$

As e is of the order of 10^{-10} esu and d of the order of 10^{-8} cm, μ is, therefore, of the order of 10^{-18} esu cm and this unit is known as the Debye (D). Dipole moment is a vector quantity and is often indicated by an arrow parallel to the line joining the points of charge and pointing towards the negative end, e.g. $\overset{+\!\longrightarrow}{\text{H}-\text{F}}$.

In general a polar bond is formed between two atoms of different radii and different electronegativities while positive centres (nuclei) of different magnitudes combine to share an electron pair. Greater the value of the dipole moment, greater is the polarity of the bond.

The following points are important regarding dipole moments:

In case a molecule contain two or more polar bonds, its dipole moment is obtained by the vertical addition of the dipole moments of the constituent bonds.

A symmetrical molecule is non-polar even though it contains polar bonds.

Disintegration series. Rutherford and Soddy found that every uranium ore which they examined contained minute quantities of radium and an appreciable amount of non-radioactive element lead. From this they concluded that uranium is the starting substance in a series of radioactive transformations which pass through radium and ultimately end in a stabla nucleus of lead. These transformations are accompanied by spontaneous emissions of alpha and beta particles resulting in the formation of new atoms. All the nuclei from the initial element to the final stable element make up a series which is called disintegration reries. Since mass numbers change only when α-particles are emmitted, the change is of 4 units at each step. The mass number of all elements in a series wlll fit into one of the formulae: $4n$, $4n+1$, $4n+2$ and $4n+3$. Thus there are four disintegration series. Neptunium or $4n+1$ series involves man made elements and other series are of naturally occurring elements.

Domain. A domain is a region in a ferromagnetic substance in which the magnetic moments of unpaired electrons are "coupled" and pointed in the same direction. The total magnetic effect is larger than if the individual moments were randomly oriented. Further, the magnetic moment of a domain can rotate to line up with an externally applied magnetic field. When all domains in a substance are aligned, the result is a powerful total magnetic effect. In addition, the domains tend to maintain their orientations unless disturbed, and thus the magnetic eflect lingers after the removal of the exteʏnal field. In other words, the material has become "magnetized."

Double salts. Compounds of the type $KAl(SO_4)_2.12H_2O$ (potassium alum). Exist only in the solid state; dissociate to ions upon dissolution in water, e.g.

$$KAl(SO_4)_2 \longrightarrow K^+ + Al^{3+} + 2SO_4^{2-}$$

Dual behaviour of water. Water can act both as an acid and a base. It acts as a base (i.e. portion acceptor) towards HCl and as an acid (i.e. porton donor) toward NH_3.

$$\underset{\text{acid}}{HCl} + \underset{\text{base}}{H_3O} \rightleftharpoons \underset{\text{acid}}{H_3O^+} + \underset{\text{base}}{Cl^-}$$

$$\underset{\text{base}}{NH_3} + \underset{\text{acid}}{H_2O} \rightarrow \underset{\text{acid}}{NH_4^+} + \underset{\text{base}}{OH^-}$$

This concept of the dual behaviour of water can be applied to explain the hydrolysis of salt solutions An aqueous solution of sodium carbonate is alkaline while salt solutions of ferric chloride, aluminium sulphate, nickel suiphate, copper nitrate, etc. are acidic because of the following reactions:

$$\underset{\text{acid}}{H_2O} + \underset{\text{base}}{CO_3^{2-}} \rightleftharpoons \underset{\text{base}}{OH^-} + \underset{\text{acid}}{HCO_3^-}$$

(carbonate is a strong porton acceptor and thus the solution becomes alkaline owing to liberation of OH^-ions).

$$\underset{\text{acid}}{[Fe(H_2O)_6]^{3+}} + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{base}}{(Fe(H_2O)_5(OH)]^{2+}} + \underset{\text{acid}}{H_2O^+}$$

$$\underset{\text{acid}}{[Al(H_2O)_6]^3} + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{base}}{[Al(H_3O)_5)OH)]^{2+}} + \underset{\text{acid}}{H_3O^+}$$

(strongly hydrated and highly charged small cation like Al^{3+} or Fe^{3+} readily gives its porion to water which can act as a base).

Aqueous solutions of NaCl, K_2SO_4, etc. are neutral because the hydrated cations are poor proton donors and the anions are poor proton acceptors.

Duralumin. (durable+aluminium). A strong lightweight alloy of aluminium with copper, magnesium, manganese, silicon, and iron. The total content of elements other than aluminium is 6 to 8 per cent.

Uses Aircraft. buses. etc.

Dusting clays. Finely divided pulverized clays that can serve as diluents and carriers in the preparation of insecticide dusts and aid in adhesion of the insecticide to foliage.

Dynamite. A mixture containing glyceryl trinitrate as its principal explosive component; usually also contains inhert (talc, tripolite) and active (charcoal, a mixture of wood powder and saltpetre) fillers. Very dangerous.

Dysprosium [Greek *dysprositos*, difficult of access] Dy. A Group III element of the 6th period of the Periodic Table of Elements, atomic number 66, atomic mass 162.50. Belongs to lanthanides. Discovered in 1886 by Lecoq de Boisbaudran. The most paramagnetic substance of all known. Valence+3.

E

Earth's crust (lithosphere). A solid outer layer of the earth about 16 km thick; the most abundant elements in earth's crust are O, Na, Si, Al, Fe, Ca, K and Mg. They form oxides, silicates, aluminium silicates, carbonates, sulphates which occur in various rocks.

Emsteinium. [After Albert Einstein, radioactive element of the actinide family, atomic number 99. The longest lived isotope is ^{259}Es ($t^{1}/_{2}$ of about 320 days). First detected in 1958 in the debries from the hydrogen bomb explosion. Resembles holmium in its chemical properties.

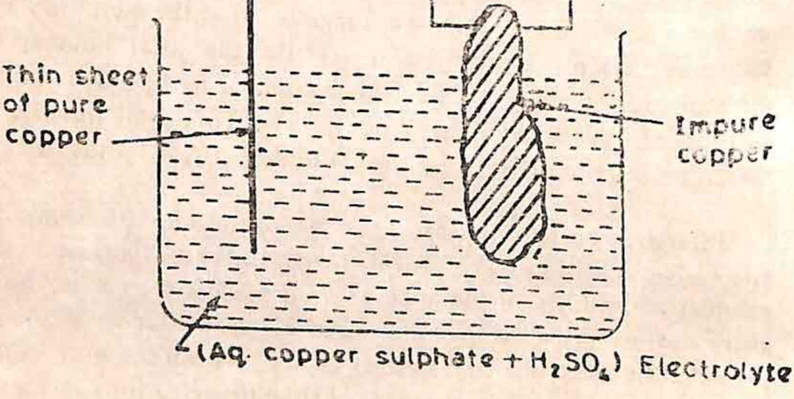
Einective atomic number (EAN) rule or Sidgwick's theory. Though Werner's theory of coordination compounds could explain the existence of complex ions and stereoisomerism in inorganic compounds, it could not be justified in the light of electronic theory. For example, a monovalent chlorine ligand was considered to satify both the primary and secondary valences. Sidgwick considered the formation of complexes by donation of an electron pair from the ligand to the metal atom or ion. Based upon this, he suggested that the metal ion will continue accepting electron pairs till the total number of electrons in the metal ion and those donated by ligands is equal to that of the next highest noble gas. This total number of electrons is called effective atomic number (EAN) of the metal.

Effective nuclear charge. In the build up of atoms by successive addition of electrons there is also an increase in the number of protons in the nucleus. Full nuclear charge is, however, not experienced by the outer electrons due to shielding provided by electrons that occupy shells between the outer shell and the nucleus. The number of shielding electrons increases from atom to atom with increasing nuclear charge. As a result, the effective nuclear charge that an outer electron experiences is not exactly the nucler charge. It can be expressed as

$$Z^{*}=Z-S$$

where Z^* is the effective nuclear charge, Z is the actual nuclear charge and S is the shielding or screening constant. Greater is the number of electrons intervening between the nucleus and the outer electrons, more will be the screening constant and hence greater will be the difference between the actual nucler charge and the effective nuclear charge.

Etectrolytic refining. It is a very convenient method for refining a large number of metals such as copper, zinc, gold, silver, etc. Here the impure metal is made anode. It is in the form of blocks. The pure metal in the form of a thin sheet acts as a cathode. They are taken in an electrolytic cell. The electrolyte used is an aqueous solution of the suitable salt of the metal. As current is passed, the pure metal from the electrolyte is deposited on the cathode and an equal amount of metal dissolved from anode passes into the solution. The impurities present in the metal ultimately settle down.


–
+
Thin sheet of pure copper
Impure copper
(Aq. copper sulphate + H_2SO_4) Electrolyte

Eleetrolytic refining of copper

Electromagnetic separation. This method can be employed only if the ore or the impurities are magnetic in nature. Here the powdered ore is taken on a belt that rolls over two heavy rollers. One of these rollers is a strong electromagnent. As the belt passes over the electromagnet, the non-magnetic particles fall off freely under the action of gravity. The magnetici mpurities remain sticking to the belt.

Electrometallurgy. A group of methods employed for the isolation and purification of metals by electrolysis at usual temperatures and electrolysis of melt or for melting metals by electrical means.

Electromotive series (Displacement series, activity series). An arrangement of the metals in the order of their activity in redox reactions (the reducing action decreases from left to right):

$$\mathrm{K > Ca > Mg > Zn > Fe > Sn > (H) > Cu > Ag > Au}$$

Any metal standing before hydrogen can displace hydrogen from acids.

Electron (e^-). A stable negatively charged elementary particle with a mass of 9.11×10^{-31} kg. Electron's charge is used as the negative charge unit. Discovered by Sir J. Thomson in 1897. Electrons are one of the constituents of the atom. Electrons moving about a nucleus form electron shells which determine the electrical, optical, and chemical properties of atoms and molecules. Electrons participating in the formation of chemical bonds are of crucial importance; these are mostly outer shell electrons (in the atoms of subgroup A elements). In the subgroups B except for IIB, atoms can also participate in bonding with their outermost but one shells.

Electron. An alloy with magnesium as the major component (about 90 per cent). Used in aircraft.

Electron affinity. It is the amount of energy released when an extra electron is added to an isolated neutral atom of an element to form a gaseous uninegative ion.

Thus,

$$\begin{array}{cccc} A & +e^{-} \rightarrow & A^{-} & +\text{Energy} \\ \text{neutral atom} & & \text{gaseous uni-} & \\ \text{(isolated)} & & \text{negative ion} & \end{array}$$

It is also equal to the amount of energy required to remove an electron from a gaseous negative ion:

$$A^{-}(g)-e^{-}\rightarrow A(g)$$

(*Note.* Usually the energy is released only in the formation of uni-negative ion. For further addition of electrons energy is needed, hence the electron affinity is negative for polynegative ion such as O^{2-}. In the formation of gaseous uninegative ion, higher is the energy given out greater is the electron affinity. Thus it is a measure of the tightness with which the electron added up is bound to the atom).

Electronegativity. It is the tendency or power of an atom to attract to itself shared pair of electrons between the bonded atoms. It is thus a measure of the ability of an atom in a molecule to attract electrons.

The concept of electronegativity is quite useful, though not quite exact. To explain the concept of electronegativity consider a molecule AB.

$$\begin{array}{ccc} A:B & A:\quad B & A:\qquad B \\ \text{(a)} & \text{(b)} & \text{(c)} \end{array}$$

In the formula (a) the electron pair is in the centre and is being shared equally between A and B. This means that both the atoms A and B have equal electronegativity.

In the formula (b) the electron pair is shifted more towards the atom A. This means the electron pair is attracted more by A than by B and hence A has greater electronegativity than B.

In the formula (c) the electron pair is shifted more towards B which means B has greater attraction for the electron pair. B has, therefore, greater electronegativity value.

Generally in a molecule of unlike atoms one is more electronegative than the other. Because of this unequal sharing the molecule develops polarity: greater the electronegativity difference greater will be the polarity of the molecule.

Enatiomorphs. Enatiomorphs (enantiomers) are pairs of molecules or complex ions which are identical in composition and structure, except that one is the mirror image of the other, and no amount of turning will permit one enantiomorph to be superimposed on the other.

Epsom salt. ($MgSO_4.7H_2O$). It is prepared from kieserite $MgSO_4.H_2O$ which is allowed to remain in contact with water until it sets to a solid mass of crystals of heptahydrote:

$$MgSO_4.H_2O + 6H_2O \longrightarrow MgSO_4.7H_2O$$

The salt is purified by recrystallization from hot water.

It is white crystalline solid with a harsh, bitter taste.

It loses water molecules on heating, e.g.

$$MgSO_4.7H_2O \xrightarrow{425\text{ K}} MgSO_4.H_2O + 6H_2O$$

$$MgSO_4.H_2O \xrightarrow{525\text{ K}} MgO + SO_3 + H_2O$$

It forms double salts as $K_2SO_4.MgSO_4.6H_2O$.

It is used for different purposes as given below:

In medicine as a purgative.

Platinised magnesium sulphate as a catalyst is used for the manufacture of sulphuric acid in Grillo process.

In fire proofing fabrics.

In weighting and sizing cotton, silk, paper, etc.

In the manufacture of soaps, ceramics, explosives, etc,

Erbium. (From Ytterby, a town in Sweden) Er. A Group III element of the 6th period of the Periodic Table of Elements, atomic number 68, atomic mass 167.26, of the lanthanide series. Discovered by Mosander in 1843. The oxidation state +3. Used in the manufacture of certain alloys, glass that effectively absorbs infrared radiation.

Europium. Eu. A Group III element of the 6th period of the Periodic Table of Elements, belongs to the lanthanide family, atomic number 63, atomic mass 151.96, a metal, has two stable isotopes, ^{151}Eu (47.77%) and ^{153}Eu (52.23%). The oxidation states in compounds +2, +3. Forms pink or pale-yellow salts.

Eutectic. [Greek *eutektos*, easily fused]. A close mixture of solids (alloy) with a melting point lower than that of any other combination of the same components. Many technological alloys heve eutetic compositions, e.g. Wood's metal, various solders, eutectic pig iron, alloys for casting. etc. Many minerals are also eutectic mixtures.

Exothermic reaction. A reaction accompanied by release of heat, as burning of coal.

F

f-Block. These are the elements in which the filling of electrons takes place in f-orbitals of an antipenultimate shell. The filling takes place progressively in $(n-2)$f orbital where n stands for the principal quantum number of the outermost shell. There are two series of f-block elements depending upon the filling of 4f or 5f orbitals. The 4f series constitutes lanthanides or rare earths from Ce (At. No. 58) to Lu (At. No. 71). The 5f series constitutes actinides from Th (At. No. 90) to Lr (At. No. 103).

In addition to incomplete antepenultimate f subshell, they also contain iucomplete penultimate d subshell. They are called f-block elements because of the regular filling of 4f (in the lanthanides) orbitals. Their general electronic configuration may be represented as $(n-2)$ f^1 to $(n-2)f^{14}$, $(n-2)$ is the antepenultimate (third from the outermost) shell. The elements belonging to the f-block of the periodic table are known as inner transition elements.

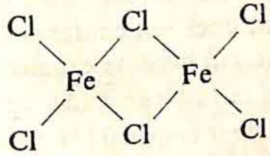
Fermium [After Fermi] **Fm.** A Group III radioactive element. atomic number 100, an actinide, discovered in 1953 in the thermonuclear explosion, in the same series of experiments as einsteinium. The longest lived isotope ^{257}Fm, $t_1/_2=79$ days. A chemical analogue of erbium, a lanthanide.

Ferric alum. A double salt of ferric sulphate and an alkali metal or ammonium sulphate. The most familiar example is ammonium ferric alum, $NH_4Fe(SO_4)_2.12H_2O$ used in tanning and dyeing.

Ferric chloride. Anhydrous ferric chloride is obtained by passing dry chlorine over heated iron scrap or wire when the salt sublimes over as deep red crystalline plates.

$$2Fe+3Cl_2 \xrightarrow{\text{heat}} Fe_2Cl_6$$

In vapour state the compound corresponds to the dimer Fe_2Cl_6 shown below:



Aqueous solution of ferric chloride is acidic because of the following hydrolysis:

$$FeCl_3+3H_2O \longrightarrow \underset{\text{(weak base)}}{Fe(OH)_3} + \underset{\text{(strong acid)}}{3HCl}$$

The formation of colloidal ferric hydroxide in the reaction imparts brown colour to the solution.

Ferric chloride is used as a laboratory reagent and in medicines. It is also used by blockmakers for etching copper and silver.

Ferromagnetism. A substance that is strongly attracted into a magnetic field ("toward a magnet") is said to be ferromagnetic. Many ferromagnetic substances retain a net overall magnetic moment ("remain magnetized") after the magnetic field has been removed. Among the elements only iron, cobalt, and nickel are ferromagnetic at room temperature. Certain compounds and alloys are also ferromagnetic.

Ferrous sulphate. Ferrous sulphate, $FeSO_4.7H_2O$ (also called green vitriol because of its light green colour) is a very important ferrous salt. It is obtained by dissolving iron in dilute sulphuric acid and concentrating the solution to crystallization.

$$Fe + H_2SO_4 \dashrightarrow FeSO + H_2$$

On large scale, it is obtained by exposing big heaps of moist iron pyrites to air when slow oxidation converts them into ferrous sulphate.

Ferrous sulphate is used as a mordant in dyeing and in tanning industries. It is also used in the manufacture of blue-black inks. Anhydrous ferrous sulphate is used in medicines when it supplements iron in diet.

Fertilizers. Growing plants obtain most of their nutrients from the soil. Since the soil does not contain an inexhaustible supply of these elements, it will become exhausted of these after repeated cultivation. Thus, in order to make up their dificiency. nutrients in the form of their compounds have to be added to the soil to make it reproductive. These substances are called fertilizers.

Essential requisites of a good fertilizer Every substance containing plant nutrients cannot be used as a fertilizer. However, the essential requisites of a good fertilizer are:

The nutrient elements present in it must be readily available to the plants.

It must be fairly soluble in water so as to enable it to dissolve in soil.

By rain or water, the fertilizer must be converted into a form which the plant can assimilate easily.

It must be stable so that it is available for a long time to the growing point.

It should not be injurious to plants.

It should be able to maintain the correct pH of the soil.

It should be cheap.

Fluorine [Latin *fluere*, to flow] F. A Group VII element of the 2nd period of the Periodic Table of Elements, atomic number 9, atomic mass 18.9984, one estable isotope, ^{19}F. First isolated by Moissan in 1886.

Properties A pale yellow gas, the most reactive of all the elements, the oxidation state in compounds—1; has the largest electron affinity. Reacts with all elements including some inert gases. Decomposes water.

$$2F_2+2H_2O \rightarrow 4HF+O_2$$

Destroys many substances, reacts with wool and rubber with ignition, reacts with most metals at room temperature (Fe, Cu, Ni are estable to fluorine because of the formation of metal flouride protecting films, and the gas is transported in special steel cyllinders).

Occurrence The chief minerals are fluorspar (fluorite), CaF_2, cryolite, Na_3AlF_6, and fluorapatite (rock phosphate) $Ca_5(PO_4)_3F$. Fluorite is used as a flux. and hence the name of the mineral and the element.

Manufacture By the electrolysis of molten KF-2HF.

Uses As an oxidizer in liquid rocket fuels, in the manufacture of UF_6 for separating the isotopes of uranium, in the manufacture of other fluorides. More widely applied in the form of its compounds such as hydrogen fluoride, aluminium fluoride, silicon fluorides, and especially fluorinated hydrocarbons.

Fluorimetry. (Luminescent analysis). The determination of substances from the intensity of fluorescence arising under UV irradiation.

Fluoroplastics. Plastic polymers of trifluorochlororthylene (fluorothene) and tetrafluoroethylene (Teflon).

Fluorspar. (Flourite) CaF_2. A mineral.

Properties Colour yellow, blue, violet, sometimes violet-black; colourless crystals occur only rarely; brittle. Usually contains impurities (rate earth elements, uranium, etc.). Pure fluorite crystals are highly transparent in the ultraviolet and infrared regions of the spectrum, give bright luminescence under calthode rays and ultraviolet irradiation, fluoresce when heated (show thermoluminescence).

Uses In metallurgy as a constitutent of law-melting slags, in the chemical indussry (source of fluorine, the manufacture of artificial cryolite and a number of fluorine compounds), in the manufacture of enamels aod glazes. Colourless trantparent crystals of fluorite are employed in optics (the manufacture of lenses). Fluorite crystals with admixture of rare earth elements and iron can be used as laser materials.

Flux. In metallurgy inorganic substances added to ores to decrease their melting points and facilitate the separation of metals from waste rock.

Francium (From France) **Fr.** A Group IA radioactive element of the 7th period of the Periodic Table of Elements. atomic number 87. Discovered in 1939 by Marguerite Perey of the Curie Institute, Paris. The only natural and longest lived isotope is ^{223}Fr. $t_1/_2=21$ min. A typical alkali metal, the closest analogue of cesium.

Freon. [The first letter from fluorine+re from refrigerant +on]. Trademark for a line of fluorinated and fluo-chlorinated hydrocarbons used as refrigerants. Made by the action of hydrogen fluoride on the corresponding hydrocarbons. Practically harmless. The most common marks are Freon-12 (CCl_2F_2) and Freon-11 (CCl_3F) used in home refrigerators, etc.

Froth flotation process. This method is chiefly used for the concentration of sulphide ores. This involves the preferential wetting of the ore by oil and gangue by water.

The ore is first crushed into the powdered form. It is then supended in water and taken in a tank. Pine oil is added. This oil acts as a frothing agent. The mixture is then agitated by blowing compressed air through it. The oil forms froth. The ore particles are wetted by oil and also rise to the surface. The impurities settle down. The froth is separated and is broken up by adding some acid. The concentrated ore is filtered, washed with water and dried.

G

Gadolinium (After J. Gadolin, Finnish chemist) **Gd.** A Group IIIA element of the 6th period of the Periodic Table of Elements, belongs to the lanthanide series, atomic number 64, atomic mass 157.25. Discovered by Maignac in 1880. Oxidation state +3, forms oxide Gd_2O_3. Gadolinium salts are colourless, gadolinium chloride, sulphate, nitrate, and acetate are soluble in water.

Galena (galenite, lead glance) **PbS.** A mineral, lead sulphide. Contains Ag, Au, and a number of other elements as admixtures. Wide-spread. Colour lead grey, not transparent. The most important lead ore, also recovered for silver and gold.

Gallium [Latin *Gallia*, France] **Ga.** A Group IIIA element of the 4th period of the Periodic Table of Elements, atomic number 31, atomic mass 69.72, two stable isotopes, ^{69}Ga (60%) and ^{71}Ga (40%), has been predicted by Mendeleev as eka-aluminium (1870). Discovered by Lecoq de Boisbaudran in 1875.

Properties silvery-white metal, m.p. 302.8 K, b.p. 2503 K. An analogue of aluminium, the oxidation state in compounds +3. Stable to air oxygen at room temperature, does not reduce water. Except for iodine, halogens react with gallium in the cold. Acids dissolve gallium at elevated temperatures. Gallium oxide, Ga_2O_3 is a white substance. Gallium hydroxide, $Ga(OH)_3$, shows amphoteric properties.

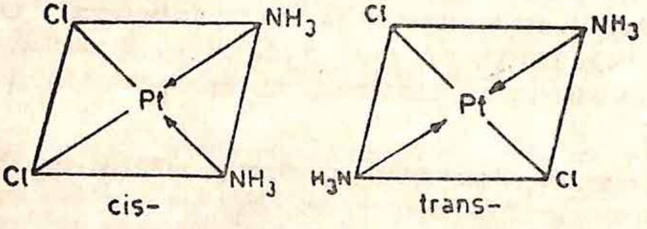
Uses Gallium and its alloys are used in high-temperature thermometres, can replace mercury in vacuum pumps. Gallium glass has high reflectivity. Gallium alloys with zinc, bismuth, cadmium, lead, and mercury have practical applications. The compounds GaAs, GaP, and GaSb are semiconductors.

Gemma ray A gamma ray is high-energy electromagnetic radiation. Gamma rays are more penetrating even than beta particles. Gamma radiation frequently accompanies other nuclear emission.

Geometrical isomerism. In this isomerism, the ligands occupy different positions around the central metal ion. If the two identical ligands occupy adjacent positions, the isomer is called a *cis*-isomer *cis* means *same* in Latin). On the other hand, when the two identical ligands are placed opposite to each other, the isomer is called a *trans* isomer (*trans* means *across* in Latin).

Geometrical isomerism ts not possible in case of the compounds with coordination number 2 or 3 and also in tetrahedral complexes (coordination number 4). This is because in these arrangements all the positions are adjacent to each other. Square planar complexes and octahedral complexes exhibit this type of isomerism. Some examples are given benlow:

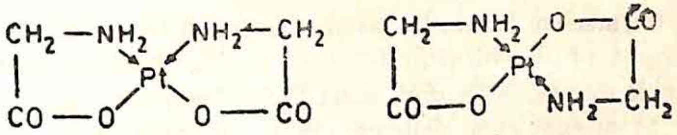
(a) $[Mx_2y_2]$ type of square plannar complexes (where x or y=monodenate ligand).



cis- trans-

Geometrical *cis*-and *trans*-)
isomers of dichlorodiammineplatinum(II)

(b) Square planar complexes having two *unsymmetrical bidentate ligands.*

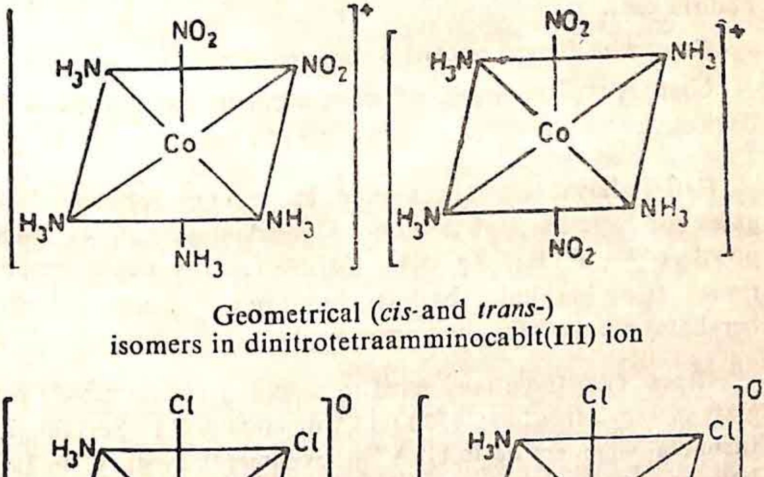


cis- trans-

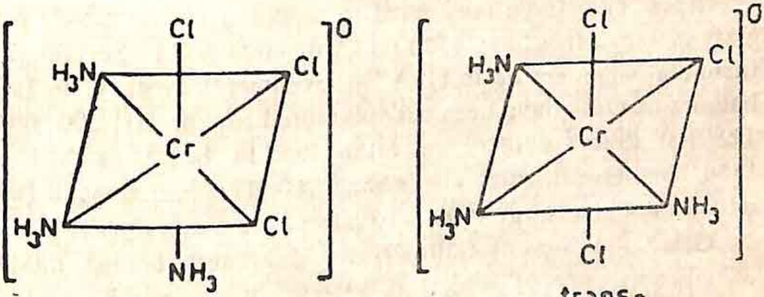
Geometrical (*cis*- and *trans*-)
isomers of diglycinatoplatinum(II)

Square planar complexes of the type [Mx_4], [Mx_3y] or [Mxy_3] do not show optical isomerism because every possible spatial arrangement of ligands arround the metal ion is alike.

(c) [Mx_4y_2] type of octahedral complexes. In *cis*-isomer the two monodentate *y* ligands are in 1 and 2-positions while in *trans*-isomer they are in 1 and 6-positions.



Geometrical (*cis*-and *trans*-)
isomers in dinitrotetraamminocablt(III) ion



cis- trans-

(d) [Mx_3y_3] type of octahedral complexes.
Geometrical (*cis*-and *trans*-)
isomers of trichlorotriamminechromium(III)

Germanium [Latin *Germania*, Germany] Ge. A Group IVA element of the 4th period of the Periodic Table of Elements, atomic number 32, atomic mass 72.59. Predicaed and described by Mendeleev as eka-silicon (1871). Discovered by Winkler in 1886.

Properties silver grey, brittle, does not yield to either hot or cold work; m.p. 1231 K. The oxidation states +4, +2 (and −4); at high temperatures, readily undergoes oxidation in the air to give oxides, GeO and GeO_2; reacts with metals to form germanides which evolve germanium (hydrides (GeH_4 etc.) under the action of HCI; easily combines with halogens; forms quite a number of organogermanium compounds.

Occurrence found in a rare mineral argyrodite, $4Ag_2S.GeS_2$, and in germanite, $Cu_3(Ge, Fe)S_4$, as admixture in zinc and tin ores.

Extraction Recovered from residues of zinc and tin ores.

Uses A typical semiconductor, used in various electronic devices.

Getter alloys. Substances used in vaccum tubes to absorb gases and vapours and to remove residual impurities. Metal powders (Ta, Ti, Ba, Zr, Nb, Ce, etc.) and various compositions (iron-barium, barium-aluminium-titanium, barium beryllate) are used for the purpose.

Glass. The Egyptians used to make artificial jewels from glass in very early time (5000 B.C. or 6000 B.C.). Several glass furnaces were set up in USA in seventeenth century. In India bangles of glass have been manufactured for the last 200 years. The first glass industry was established in Buldhana (M.P.) in 1856. At present there are about 100 glass industries in India which produce about 400000 tonnes of glass every year.

Glass is a non-cystalline transparent supercooled mixture of silicates, one of which is always of an alkali metal. Its composition varies with different varieties of glass. An approximate formula for ordinary glass may be given as:

$$M_2O.M'O.6SiO_2$$

where M=Na or K and M'=Ba, Zn or Pb

Gold. Gold occurs free in nature and in the minerals calaverite, sylvanite, petzite and nagyagite. Sea water contains 0.004 ppb of gold and the earth's crust contains about 0.005 ppm. The adult human body contains <10 mg gold. Gold is not normally present in plant tissues and it is not an essential nutrient. Using neutron activation analysis, the concentration of gold has been found 22 ug/mL and 0.4 ug/mL in milk and infant urine respectively. The concentration of the metal in the skin and nails was higher than in the plasma.

Gold exhibits valences of $+1$ and $+3$, and forms both cationic and anionic complex salts such as chloroaurates. Simple Au^+ and Au^{3+} ions donot exist in solution, but double salts such as gold-sodium thiosulphate $[AuNa_3(S_2O_3)_2]$ are both stable and water soluble. Au has strong affinity for S, weak affinity for C and N, and no affinity for O; only in usual types of chelate formation does Au complexes with oxygen. Gold readily complexes with sulphur-containing ligands.

Owing to its poor absorption, gold dust and insoluble salts of gold are not toxic when given orally. However, soluble gold compounds are toxic, The toxicity of simple cationic Au is less than that of the more soluble double salts or organic salts. From the biochemical view point, gold is not considered an essential element It is considered a substance with toxic potential, however, gold used in jewellery and coinage now has new application in the coating for space satellities and space suits, where it serves as a reflector of radiation. The Chinese were probably the first to use gold in medicine. Alchemists attempted to prepare "an elixir of life" from gold to cure all ills and confere eternal youth. Gold salts are used therapeutically in rheumatoid arthritis and syphills, and gold alloys in dentistry. Gold is also used sporadically in treating tuberculsis. The pharmacology of gold in patients and experimental animals has been extensively studied in the past. Biochemically, gold is indeed a rare metal. Radioactive gold has application in the treatment of cancer. Gold leaf serves as a light porous, dry dressing and increases the vascularity of the application site. Because of the malleability of the Au alloys used in dental prosthesees, there is only negligible loss from wear in gold fillings over many years. Gold is also used in electronics for contacts, printed circuits, connections, precision resistances, and semi-conductors. The space industry utilises gold in glass to metal seals, as a coating on bearings and as a coating against infra-red and high intensity solar radiations Gold surfaces also resist corrosion.

Colorimetricmethods for the determination of gold are fairly sensitive but are subject to interferences. For example, the diethylaminobenzylidene rhodamine-gold complex has a detection sensitivity of 0.01 μg/mL and the isopropyl ether extract-of rhodamine B, 3 μg/mL, Extraction of gold from an acidic solution could be utilized in isolating the element for analysis by various instrumental means.

The fluorescence of the gold-rhodamine B complex has been utilized in gold determinations. A detection sensitivity of 0.5 μg/mL has been reported for the complex. There are intereferences, however, since rhodamine forms fluorescent complex with cobalt, iron, mercury, manganese, tin, antimony and thallium, among others.

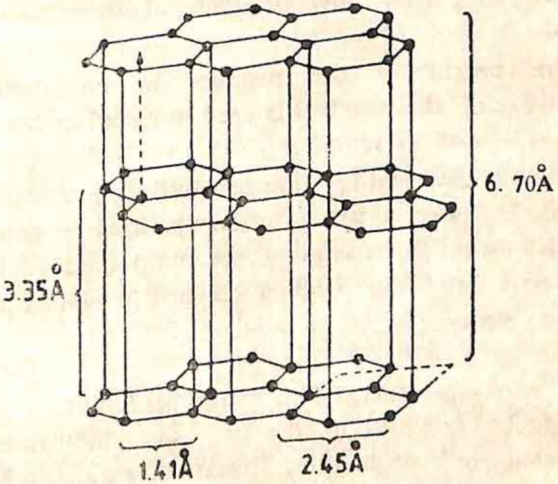
Paper chrmatography has been employed to separate gold from platinum metals. Thin layer chromatography could also be applied. Charcoal has been used as an adsorbent in determining gold in steam waters. Ethyl cellulose was found to be useful absorbent in gold analysis.

Spectrographic methods were the earliest of instrumental techniques applied in measuring gold concentrations in biological materials. Few applications of neutron activation analysis to the determination of gold in biological materials have been used, but the technique has been utilised in analyzing rocks and ores for the metal. Recently, an X-ray fluorescence spectroppotometric procedure for gold analysis in biological fluids has been described.

Detection limits for gold through AAS at 243.0 nm resonance line are found to be about 0.05 μg/mL; very favourable detection limits indeed for analysis of biological materials from patients receiving chrysotherapy. Many reports of flame atomic absorption analysis of serum and urine have appeared since the instrumentation became available. Methods describing applications of flameless atomization have been reported. Gold in urine is precipitated out as a telluride, dissolved in aqua regia and extracted into methylisobutyl ketone prior to analysis in the graphite furance.

Although XRF and AAS methods are very convenient from the analyst's point of view but the accessibility of the instrumental facility to a common analyst/chemist becomes a hurdle in the choice and one looks for some alternate instrument and method. Spectrophotometric methods then become the methods of choice. Spectrophotometric procedures are popular, commonly employing dithizone (diphenylthiocarbazone) and rhodamine B to develop complexes absorbing at 500 nm and 565 nm respectively.

Graphite. In graphite carbon atoms are linked to the other carbon atoms by covalent bonds, forming hexagonal rings. The layers of carbon atom hexagons are arranged one over the other and are held together by weak attractive forces which account for the softness of graphite.



The layer structure of graphite

It is soft grey solid with a metallic lustre.

It is a good eonductor of heat and electricity.

Its specific gravity is 2.25.

It is stable even at high temperatures. Its melting point is 3937 K.

It is used as a dry lubricant.

Due to higher melting point, it is used for making crucibles.

It is used in making pencil leads.

For making electrodes (being a good conductor of electricity).

Gravimetric analysis. Perhaps the most important of the classical methods of analysis are the gravimetric methods which are based upon obtaining the weight of a precipitate. In general, a gravimetric method of analysis consists of the following steps:

The sample weight is determined and it is dissolved in a proper solvent.

A sequence of chemical reactions is carried out to obtain a suitable product.

The weight of the product of the reactions is determined.

The weight of the product in conjunction with the knowledge of the product is used to calculate the quantitative composition of the sample.

The key chemical reaction involved in gravimetric methods is almost always a precipitation, because it can be a highly selective means for separating the component of interest from the matrix, and the product weighed is almost always a precieptate, because it can be weighed readily.

Gravity separation. This method is based on the difference in specific gravities of the ore and the impurities. The powdered ore is washed in a stream of water on Wilfley tables. The lighter rocky and other impurities are washed away leaving behind heavier ore particles.

Greenhouse effect. The gaseous envelope surrounding the earth is the atmosphere. The atmosphere is a mixture of gases. Nitrogen makes up almost four-fifths of it and oxygen being a little more than a fifth. Small quantities of other gases like argon, helium, neon, krypton, xenon, carbon, dioxide, hydrogen and ozone are also present. The atmosphere also contains considerable quantity of water vapour which is due to evaporation from rivers, lakes, oceans, etc. This atmosphere is retained on the earth by gravitation attraction and a large measure rotates with it.

The earth's atmosphere acts as the glass walls and roofs of a greenhouse in trapping heat from the sun. This is what is known as the "Greenhouse Effect". The atmosphere moderates the extremes of heat and cold upon the earth. It is due to the greenhouse effect of the atmosphere that the change in temperature between day and night and similarly between summer and winter is reduced. The heat rays from the sun penetrate the air and warm the earth's surface during the day.

The overlaying atmosphere traps this heat so that it escapes more slowly into space, moderating the cold of night. Compare this situation with that at the moon, there is practically no atmosphere. The moon becomes very hot during the lunar day (the temperature reaches boiling point of water) and on lunar night the temperature falls below even 170 K. Had there been no atmosphere on the earth, we would have also suffered similar extreme conditions.

It will be interesting to note the extent of energy radiated by the sun and the extent to which it is moderated by atmosphere. Energy is radiated from the sun at the rate of about 43,000 kW per square metre of solar surface. Solar radiation which falls on a surface normal to the sun's rays at the outer limit of the earth's atmosphere has an an average intensity of 2(±2%) cal. per minute per square centimetre (1.41 kW per squre metre). This quantity is known as solar constant and it has remained virtually the same for several billion years. Only about 46 per cent of the in coming solar energy actually reaches the earth's surface, since, on the average, 35 per cent is reflected back into space by cloud and the remaining 19 per cent is absorbed by the atmosphere. The total amount of solar energy which reaches earth is nearly 7×10^{17} kW-hr per year which is more than 30,000 times as much as that used in all man-made devices. Such huge amount of incoming energy warms the earth and produces, through photosynthesis, all of the food, fuel, and oxygen upon which life depends.

The earth's atmosphere is being polluted by many gases notably carbon dioxide which is produced by burning of coal, and other fossil fuels. Like the glass roof of a greenhouse, carbon dioxide in the atmosphere is transparent to short-wave radiant energy from the sun, but tends to block the long-wave heat energy radiated outward from the earth. Thus an increase in atmospheric carbon dioxide holds more heat in the atmosphere, raising the earth's average temperature.

The world scientists believe that the world-wide temperatures will rise dramatically in the next century, with severe effects in weather and climate, unless mankind reduces its dependence on fossil fuels. The carbon dioxide trapes heat which would otherwise escape and thus warms the surface of the earth. This will make the earth more humid, forest land will shrink and sea levels will rise, flooding many low-lying areas.

The earth's temperatures have risen one to 2.5 degrees centigrade since 1850 but now are rising 02. to 0.5 degrees per decade. Some scientists have warned that this trend would melt the polar ice caps and raise the level of water in the oceans. Even a 300 mm rise would give problems to many areas. Many large low-lying areas will become more vulnerable to storm-blown waves.

It has been predicted that in the next 20 years earth will become warmer than it has been in the past 100,000 years and their will be major practical impacts of such a warming, although little research has been done to define these impacts. Scientists, therefore, recommend that alternative sources of energy should be developed and use of fossil fuels should come down.

Group displacement law. In radioactive decay when an atom emits a β-particle, its atomic number is increased by one unit and if it emits an α-particle ($_2$He), its atomic number is decreased by two units. The new atoms formed as a result of β- or α-emissions occupy new positions in the Periodic Table depending upon the type of radiations. This displacement of positions in the Periodic Table on account of β- and α-particle is known as group displacement law.

H

Hafnium. Hafnium belongs to the group IVB of the Periodic Table along with titanium and zirconium. It is a d-block element having the configuration [Xe] $4f^{14}$ $5d^2$ $6s^2$. Its properties are similar to zirconium because of the lanthanide contraction. There is also very close resemblance between the compounds of these two elements.

It occurs in zirconium minerals. Actually, it was first discovered in these minerals by X-ray methods. In the earth's crust, it occurs to the extent of 0.002 per cent. Its richest minerals are alvite which is zirconium, thorium-hafnium orthosilicate (Zr, Th, Hf) SiO_4, malacone, nageite, etc.

Zircon contains about 0.5 - 2.0% hafnium and all extraction methods for zirconium also lead to the extraction of hafnium. As the chemistry of these two-metals is so similar that no direct chemical method can be employed for their separation and independent extraction. The only way lies in their slight difference in extraction behaviour or in their solubility of their compounds. Different methods given so far are as follows:

Fractional crystallization of the double fluorides It is possible to get reasonable separation by repeated crystallization of the double fluorides from water. The solubilities of $(NH_4)_2[ZrF_6]$ and $(NH_4)_2[HfF_6]$ in water are given below (in moles/litre):

$(NH_4)_2ZrF_6$	0.611	at 273 K
$(NH_4)_2HfF_6$	0.891	at 273 K

In practice, the mineral is fused with potassium hydrofluoride and hexafluo-zirconate and hexafluohafanate are separated from each other due to difference in their solubility.

Fractional crystallization method is now-a-days replaced by ion-exchange and solvent exchange methods.

Extraction of zirconyl chloride with thiocyanate-rich methyl isobutyl ketone (MIBK) Crude zirconyl chloride ($ZrOCl_2$) is treated with counter current stream of thiocyanate rich methyl isobutyl ketone. Hafnyl chloride goes into the MIBK. Hafnium is preferentially extracted being contaminated with less than 2 per cent zirconium. MIBK extract is then treated with HCl and then with H_2SO_4. By this treatment hafnium is brought into the aqueous layer. It is then precipitated with NH_4OH which on ignition yields oxide. The unextracted zirconium is recovered as ZrO_2.

Elution of the extra chlorides from silica gel column Anhydrous methanol solution of the tetrachloride of Zr and Hf is passed through a silica gel column. The fixed chlorides are then washed first with 2 N HCl in methanol which removes $ZrCl_4$. Finally elution is done with 7 N H_2SO_4 which removes $HfCl_4$.

Ion-exchange method The best method for separating zirconium and hafnium is based on the application of ion-exchange method. In this method, a mixture of $(NH_4)_2ZrF_6$ and $(NH_4)_2HfF_6$ is passed through an ion-exchange resin of the type $[RNMe_3]Cl$ when the hexafluoroanions of zirconium and hafnium are absorbed by the resin but at a different capacity. Then the absorbed anions are eluted with an aqueous mixture of HF and HCl which releases the hexafluoroanions from the resin. The anions, so formed, are eluted one after the other.

$$2[RNMe_3]Cl+(NH_4)_2ZrF_6 \rightarrow [RNMe_3]ZrF_6+2NH_4Cl$$

$$2[RNMe_3]Cl+(NH_4)_2HfF_6 \rightarrow [RNMe_3]_2HfF_6+2NH_4Cl$$

$$[RNMe_3]_2ZrF_6+HCl \rightarrow H_2ZrF_6+2[RNMe_3]Cl$$

$$[RNMe_3]_2HfF_6+2HCl \rightarrow H_2HfF_6+2[RNMe_3]Cl$$

Like zirconium, hafnium is obtained by the following methods:

By reducing the oxide with carbon, sodium, calcium or magnesium.

$$HfO_2+2C \rightarrow 2CO+Hf$$

By reducing the tetrachloride with sodium or magnesium.

$$HfCl_4+4Na \rightarrow Hf+4NaCl$$

By the thermal decomposition of the tetra-iodide over a heated tungeten filament (Van Arkel method).

$$HfI_4 \xrightarrow[\text{tungsten filament}]{\text{decomposition over a}} Hf+2I_2$$

Like zirconium, hafnium is silvery white, hard, high melting. Its chemical properties have been found to be similar to those of zirconium.

Like zirconium, hafnium forms the compounds such as HfO_2, HfX_4, HfC, etc. Their preparations and properites are quite similar to the corresponding zirconium compounds.

At high tempreature, hafnium forms dioxide and nitride.

It is unaffected by cold water but it decomposes steam forming HfO_2.

$$Hf+2H_2O \rightarrow HfO_2+2H_2$$

It is unaffected by cold or hot dilute and concentrated HCl. However, vapours of HCl affack the metal to for $HfCl_4$.

$$Hf+4HCl \rightarrow HfCl_4+2H_2$$

Dilute H_2SO_4 has no action on it but hot H_2SO_4 (60 per cent) reacts with it liberating SO_2. Hafnium dissolves in hydrofluoric acid in aqua regia.

It is not attached by alkali solutions of ordinary preparations but when fused with alkalis in the presence of air, it forms Na_2HfO_3.

$$Hf + 2NaOH + 1/2 O_2 \rightarrow Na_2HfO_3 + H_2$$

In controst to zirconium, hafnium is a strong neutron absorber and is used as a control rod material for nuclear reactors. It is used in alloys with tungsten and tantalum. It is also used in electronics as cathodes of television tubes.

Half-life period. Half-life period of a radioactive element may be defined as that time during which its concentration becomes exactly one-half of its original concentration. In other words, it is the time required for the decay or disintegration of one-half of the original amount of a radioactive substance. It is denoted by $t_1/_2$.

Half-life period of a radioactive element is an immediate answer to the rate of decay, i.e. it provides information whether a unclear disintegration is slow or fast. Half life period of a radioactive element does not depend upon the intitial amount of the radioactive element present but only depends upon the radioactive constant λ.

The statement that half-life of ^{14}C is 5600 years implies that any given 'amount of ^{14}C will become exactly one-half after 5600 years.

Halic acids, HXO_3. These acids are prepared by the action of dilute sulphurie acid on barium halate.

$$Ba(XO_3)_2 + H_2SO_4 \rightarrow BaSO_4 + 2HXO_3$$

Bromic acid and iodic acid can be prepared by the oxidation of bromine and iodine respectively as:

$$X_2 + 5Cl_2 + 6H_2O \rightarrow 2HXO_3 + 10HCl \qquad (X = Br, I)$$
$$I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

These acids are colourless liquids but iodic acid is solid. The thermal stability of the acids increases with increase in the atomic number, e.g. $HClO_3$ is stable in dark and decomposes in light. $HBrO_3$ decomposes on concentration above 50 per cent and HIO_3 decomposes above 473 K.

$$3HClO_3 \rightarrow HClO_4 + Cl_2 + 2O_2 + H_2O$$
$$4HBrO_3 \rightarrow 2Br_2 + 5O_2 + 2H_2O$$
$$2HIO_4 \rightarrow I_2O_5 + H_2O$$

These acids are oxidizing agents. Oxidizing character decreases with increase in atomic number. Chloric acid attacks organic substances and dissolves certain metals to form the metal chlorates. Other halic acids oxidize hydrogen sulphide to sulphur, sulphur dioxide to sulphuric acid, etc.

$$2HXO_4 + 5H_2S \rightarrow X_2 + 5S + 6H_2O \qquad (X = Br, I)$$
$$HXO_3 + 5HX \rightarrow 3X_2 + 3H_2O$$

Halogens [Greek *hals, halos,* salt+*genes,* born]. The chemical elements of Group VIIA of the Periodic Table of Elements: fluorine, F; chlorine, Cl; bromine, Br; iodine, I and astatine. At. All halogens are strong oxidants. In passing from F to At, the reactivity of halogens decreases and that of halide ions, F^-, Cl^-, Br^-, I^-, increases.

Halous acids, HXO_2. Only chlorine forms such type of acid in solution which is known as chlorous acid, $HClO_2$ and its salts are known as chlorites. The chorite ion appears to be stable.

A chlorite is obtained by the action of chlorine dioxide on alkalis or peroxides.

$$2KOH + 2ClO_2 \rightarrow KClO_2 + KClO_3 + H_2O$$
$$Na_2O_2 + 2ClO_2 \rightarrow 2NaClO_2 + O_2$$

Chlorous acid is prepared by the reaction of chlorites with dilute acids.

$$Ba(ClO_2)_2 + H_2SO_4 \rightarrow BaSO_4 + 2HClO_2$$

Chlorous acid and chlorites liberate iodine from iodides.

$$4I^- + ClO_2^- + 2HO \rightarrow 4OH^- + Cl^- + 2I_2$$

Chlorous acid undergoes auto-oxidation at room temperature.

$$2HClO_2 \rightarrow HOCl + HClO_3$$

Hard and soft acids and bases (HSAB). Arland, Chatt and Davis (1958) categoized the metal ions and the ligands into two classes:

Class (*a*) It includes ions of alkali metals, alkaline earth metals, lighter transition metals in higher oxidation states such as Ti^{4+}, Cr^{3+}, Fe^{3+} and Co^{3+}, and the hydrogen ion, H^+. Small size, high polarizing power and high positive oxidation state are the characteristic features of these ions. Their outer electrons or orbitals are not easily distorted. The ligands which preferably combine with these ions are also placed in class (a). For example, the ligands NH_3, R_3N, H_2O and F^- ion have great tendency to coordinate with class (a) metal ions (Be^{2+} Co^{3+}, Ti^{4+}, etc.) and thus they belong to this class. The tendency of the complexation of the ligands with class (a) metal ions follows the order:

$$\mathrm{F > Cl > Br > 1}$$
$$\mathrm{O > S > Se > Te}$$
$$\mathrm{N > P > As > Sb}$$

Class (*b*) It includes ions of the heavier transition metals and those in lower oxidation states such as Cu^+, Ag^+, Hg^{2+} Pd^{2+}, Pt^{2+} and Mg^{2+}. They are large sized and their outer electrons or orbitals are easily distorted. The ligands which have preferences towards these metal ions also belong to this category. For instance, ligands such as R_3P (phosphines) and R_2S (thioethers) prefer to combine with Pd^{2+}, Pt^{2+}, and Hg^{2+}. The complexing ability of the ligands for the metal ions of class (b) follows the order:

$$\mathrm{F < Cl < Br < 1}$$
$$\mathrm{G < S < Se \sim Te}$$
$$\mathrm{N < P > As > Sb}$$

Pearson (1963) changed the terminology and gave the names hard and soft to the members (metal ions and ligands) of class (a) and class (b) respectively. Thus, in his classification, metal ions of class (a) become hard acids and the ligands of this class become hard bases (Tables given). On the other hand, metal ions and the ligands of class (b) become soft acids and soft bases respectively (Tables given). It can be seen from the tables that the classification is not very rigid and there are borderline acids and bases as well.

Classification of Acids

Hard acids	Borderline acids	Soft acids
H^+, Li^+, Na^+, K^+, (Rb^+, Cs^+)	Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}	$Co(CN_5{}^{3-}$,Pd^{2+}, Pt^{2+}, Pt^{4+}
Be^{2+}, $Be(CH_3)_2$, Mg^{2+},	Rh^{3+}, Ir^{3+}, Ru^{3+},	Cu^+, Ag^+, Au^+. Cd^{2+},
Ca^{2+}, Sr^{2+}, Ba^{2+}	Os^{2+}	$Hg_2{}^{2+}$, Hg^{2+}, CH_3Hg^+
Sc^{3+}, La^{3+}, Ce^{4+}, Gd^{3+},	$B(CH_3)_3$, GaH_3	BH_3, $Ga(CH_3)_3$, $GaCl_3$,
Lu^{3+}, Th^{4+}, U^{4+}, $UO_2{}^{2+}$ Pu^{4+}	R_3C^+, $C_6H_5{}^+$, Sn^{2+}, Pb^{2+}	$GaBr_3$, GaI_3, Ti^+, $Tl(CH_3)_3$
Ti^{3+}, Zr^{4+}, Hf^{4+}, VO^{2+}	NO^+, Sb^{3+}, Bi^{3+}	CH_2, carbenes
Cr^{3+}, Cr^{6+}, MoO^{3+}, WO^{4+}, Mn^{2+}, Mn^{7+}, Fe^{3+}, Co^{3+}	SO_2	τ-acceptors: trinitrobenzene, chloranil, quinones, tetracyanoethylene, etc.
BF_3, BCl_3, $B(OR)_3$, Al^{3+},		HO^+, RO^+, RS^+, RSe^+, Te^{4+}, RTe^+,
$Al(CH_3)_3$. $AlCl_3$, AlH_3, Ga^{3+}, In^{3+}		
CO_2, RCO^+, NC^+, Si^{4+}, Sn^{4+}, CH_3Sn^{3+}, $(CH_3)_2Sn^{2+}$		Br_2, Br^+, I_2, I^+, ICN, etc.
N^{3+}, $RPO_2{}^+$, $ROPO_2{}^+$, As^{3+}		O, Cl, Br, I, N, RO°, RO°$_2$,
SO_3, $RSO_2{}^+$, $ROSO_2{}^+$		*M*° (metal atoms) and bulk metals
Cl^{3+}, Cl^{7+}, I^{5+}, I^{7+}		
H*X* (hydrogen-bonding molecules)		

Classification of Bases

Hard bases	Borderline cases	Soft bases
NH_3, RNH_2, N_2H_4	$C_6H_5NH_2$, C_5H_5N, N_3^-, N_2	H^-
H_2O, OH^-, O^{2-}, ROH, RO^-, R_2O	NO_2^-, SO_3^{2-}	R^-, C_2H_4, C_6H_6, CN^-, RNC, CO
CH_3COO^-, CO_3^{2-} NO_3^-, PO_4^{3-} SO_4^{2-}, ClO_4^-	Br^-	SCN^-, R_3P, $(RO)_3P$, R_3As (R_2S, RSH, RS^-, $S_2O_3^{2-}$
F^-, (Cl^-)		I^-

Hardening. It is the process of heating steel to bright redness and then cooling sudenly by plunging in oil or water (Quenching). Steel so treated is hard and brittle.

Heisenberg's uncrtainty principle. The Heisenberg uncertainty principle states that it is impossible to know simultaneously both the momentum and the position of a particle with certainty. This means that as a measurement of momentum of particle is made more precisely, a measurement of the position of the particle is correspondingly less precise. Similarly if the position is known precisely, the momentum must be less well known. There are several ways of expressing the uncertainty principle in the form of an equation. One simple form is as follows.

In the case of an electrom, if Δx is the uncertainty in the measurement of position and Δp is the uncertainty in the measurement of momentum the relationship proposed by Heisenberg is

$$\Delta p . \Delta x \geqslant \frac{h}{4\pi}$$

where h is Planck's constant.

Thus if $\triangle x$ is small, that is the position of the particle is known more or less exactly, $\triangle p$ will become large, or there would be large uncertainty regarding momentum. Similarly, if an attempt is made to measure exactly the velocity, the $\triangle x$ will become large.

Helium [Greek *helios*, the sun] **He.** A zero Group element of the 1st period of the Periodic Table of Elements, atomic mumber 2, atomic mass 4.0026. Natural helium contains two stable isotopes, ^{3}He and ^{4}He, the latter being by far more abundant. First isolated by Ramsay from the radioactive mineral, uraninite (1895).

Properties A monoatomic gas, chemically inert, colourless and odourless, b.p. 4.1 K. The helium atom consists of the nucleus and two electrons. The nucleus is very stable, it is formed in nuclear reactions.

Occurrence Constitutes 0.0005% of earth's atmosphere, present in the atmospheres of the sun and stars. Formed and accumulated in radioactive minerals undergoing alpha-decay.

Extraction From natural gases containing helium.

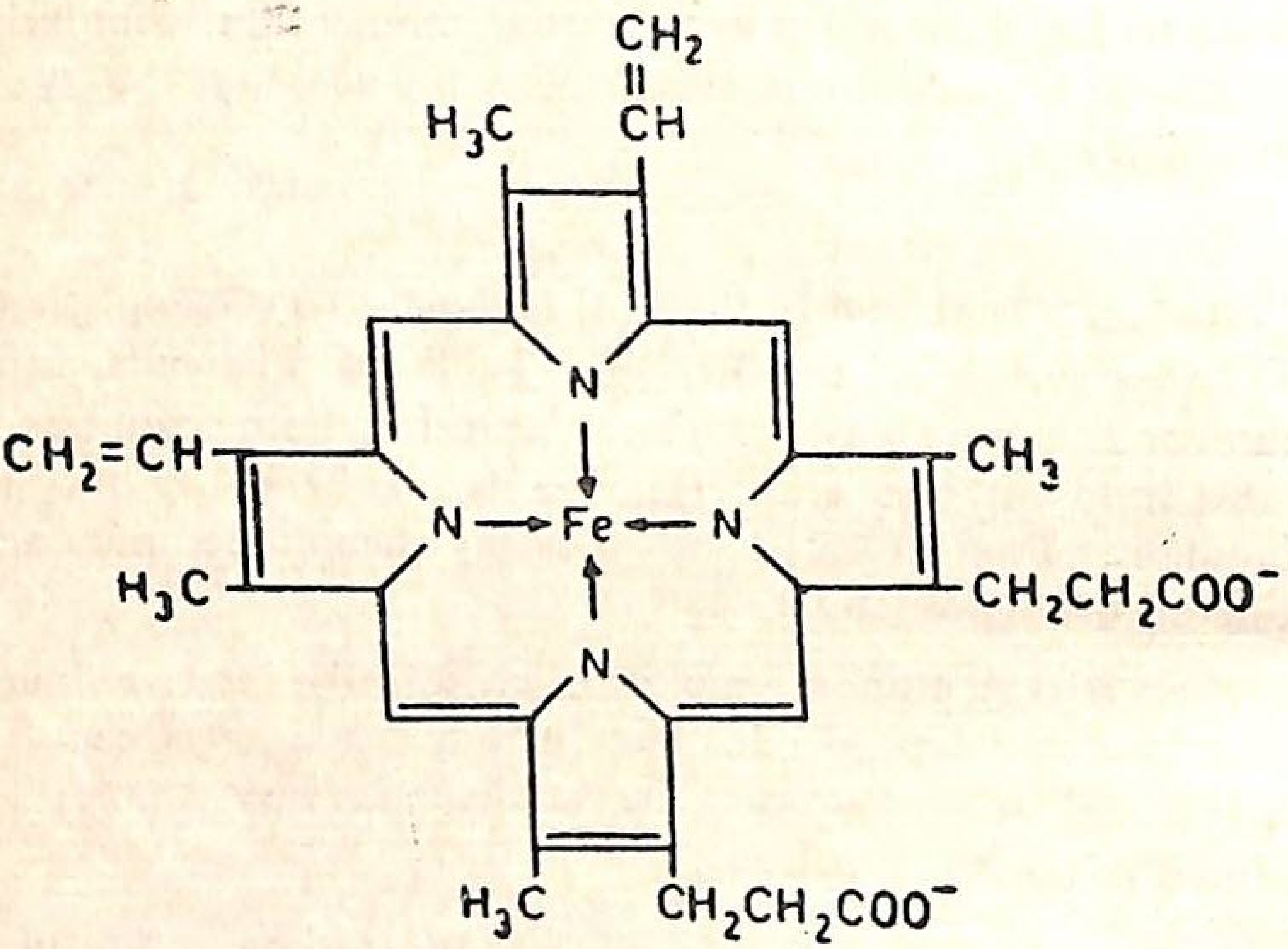
Uses Used in cyostats for deep cooling, as inert shield in metallurgy (arc welding) and scientifi work, in nuclear encineering. Liquid helium is colourless fiuid used in physicochemical experiments carried out at very low temperatures.

Hematite. One of the chief ores of iron, Fe_2O_3, widely distributed in nature. Colour black to dark-steel and cherry-red.

Varieties Iron glance, red hematite, etc. Can be prepared synthetically.

Uses Smelting of pig iron, in the manufacture of lacquers and dyes as a mineral pigment (iron minium), as a pigment in oilcloth, linoleum. red pencils, polygraphy, stable coloured enamels. Also used for decorative purposes.

Heme.



Holmium. (Latin *Holmia*, Latinized form of Stockholm) **Ho.** A Group III element of the 6th period of the Periodic Table of Elements, atomic number 67, atomic mass 164.93: a lanthanide. Discovered in 1879 by Cleve. The oxidation state in compounds +3. Holmium oxide and holmium salts are yellow.

Hybridization. It is defined as the process of mixing the orbitals of same or nearly the same energies to give rise to a new set of orbitals which are identical in all respeets. The new set of orbitals are called the hybrid orbitals and the phenomenon is known as hybridization. The number of hybrid orbitals produced is equal to the number of atomic orbitals used for mixing.

Hydrate. A compound containing water molecules is a hydrate. The water molecules may or may not be bound to specific atoms or ions in the crystalline solid.

Hydrate isomerism. This type of isomerism arises out of different disposition of water molecules inside and outside the coordination sphere. For example, the compound $[CrCl_3.6H_2O]$ exists in three hydrate isomers, viz. volet coloured $[Cr(H_2O)_6]Cl_3$ and green coloured

$[Cr(H_2O)_5Cl_2.H_2O$ and $[Cr(H_2O)_4Cl_2]Cl.2H_2O$.

Some more examples are:

$[Cr(en)_2H_2O)_2]Br_3$ and $[Cr(en)_3(H_2O)Br_2]Br.H_2O$
$[Co(NH_3)_4(H_2O)Cl]Br_2$ and $[Co(NH_3)_4Br_2]Cl.H_3O$

Hydride. A compound containing hydrogen bonded to a less electronegative element is called a hydride, In such compounds the hydrogen is assigned a —1 oxidation state. All hydrides do not contain the hydride ion, H^-.

Hydrogen. [Greek *hydor* water+*genes*, born] **H.** The first element of the Periodic Table of Elements, atomic mass 1.00797. Discovered in 1766 by Cavendish. Contains three isotopes, protium (^1H), deuterium (D or ^2H), and tritium (T or ^3H). The hydrogen atom contains one electron, the molecule two atoms linked by a covalent bond.

Properties A gas, the oxidation stales in compounds +1 and —1. An effective reducing agent. Not very reactive under usual conditions, combines directly only with the most active non-metals (with fluorine; with chlorine reacts in the light). At elevated temperatures, reacts with many elements. The reaction with fluorine develops as explosion, with chlorine and bromine goes in the light or under heating, with iodine only at elevated temperatures. Combines with nitrogen in the presence of a catatyst to give ammonia. The reaction of hydrogen with carbon monoxide, CO, is of practical importance as a route to hydrocarbons, alcohols, aldehydes, etc. Combines directly with alkali and alkaline earth metals to produce metal hydrides (NaH, CaH_2, etc.)

Occurrence Widely distributed in nature, constitutes 1 per cent of the mass of earth's crust. The most abundant element in the universe, prevails in the sun and most stars constituting up to one half of their mass.

Uses In the synthesis of NH_3.HCl, methanol manufacture (in the reaction with CO), welding and cutting metals, the hydrogenation of solid and liquid fuels, fats, and various organic substances, etc. Deuterium and tritium are used in the nuclear industry.

Hydrogenation reaction. A reaction which consists of the addition of one or more hydrgen molecules to another molecule is termed a hydrogenation reaction.

Hydrogen bomb. The nuclei of light elements have a lower binding energy than that for elements of intermediate mass. They are therefore less stable; consequently the fission of two light elements results in a more stable nucleus. The process of nuclear fusion also liberates energy, and as a matter of fact, for a given weight of material more energy is liberated by fission of light nuclei than by fission of heavy nuclei, e.g. in the following fusion reaction: $^7Li + {}^1H \longrightarrow 2\,{}^4He$ the loss of mass is about 0.231per cent whereas the loss of mass in fission of uranium-235 is about 0.1 per cent only, and consequentiy a very much larger amount of energy is relased in nuclear fusion.

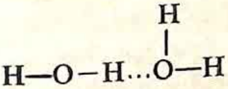
The fusion of light nuclei needs a very high temperature, and is called thermonuclear reaction. The thermonuclear reaction is accompained by release of a colossal amount of energy. Nuclear reaction may take place at the high temperature of many million degrees that develops during explosion of an atom bomb. At the high temperature available by the fission of uranium or plutonium, the nuclei of light atoms are greatly accelerated to overcome their potential barrier and enter into a fusion reaction. A mixture of deuterium and tritium surrounding an atom bomb will undergo nuclear fusion; ^2H (deuterium) $+ {}^3H$ (tritium)$\rightarrow {}^4He + {}^1n$ at the high temperature caused by the detonation of the atom bomb. Hydrogen bomb is made in this way. It may be one thousand times as powerful as an atom bomb, and one hydrogen bomb can destroy any city in the world. Deuterium for hydrogen bomb is obtained from the fractionation of water, and tritium is obtained by the reaction,

$$^{6}Li + {}^{1}n \rightarrow {}^{3}H + {}^{4}He$$

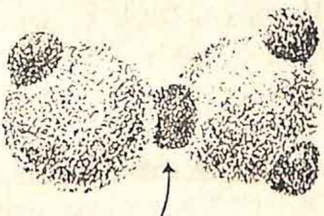
Hydrogen bond. It is a strong dipole-dipole interaction which arises from the property of a hydrogen atom to act as bridge between two highly negative atoms. This bridge of hydrogen holds one of the two highly negative atoms by a covalent bond and the other by a weak electrostatic force. Whenever a substance contains a hydrogen atom linked to highly electronegative atom such as F, O or N, the latter attracts the pair of electrons more and becomes slightly negative whereas the hydrogen atom becomes slightly positive. For example, in a molecule of water O—H is a covalent bond. The highly electronegative oxygen attracts the shared pair nearer to it and acquires a slight negative charge while hydrogen becomes slightly positive.

$$H—\overset{-\delta}{O}: \quad \overset{+\delta}{H}$$

When two molecules of water come nearer, slight negatively charged oxygen attracts the positive charge of hydrogen atom of the second molecule and a weak bond is established. The attractive force is known as hydrogen bond and is represented by a dotted line.



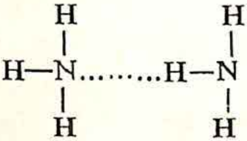
$$H—O—H \cdots \overset{\overset{\displaystyle H}{|}}{O}—H$$



Hydrogen bond

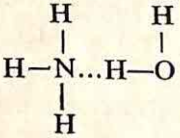
Some more examples of hydrogen bonding are shown below:

$H-F \ldots H-F$
Hydrogen fluoride



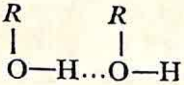
$$\begin{array}{ccccc} & H & & & H\\ & | & & & |\\ H- & N & \cdots\cdots & H- & N\\ & | & & & |\\ & H & & & H\end{array}$$

Ammonia



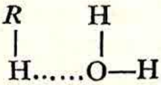
$$\begin{array}{ccccc} & H & & & H\\ & | & & & |\\ H- & N & \cdots & H- & O\\ & | & & & \\ & H & & & \end{array}$$

Ammonium hydroxide



$$\begin{array}{ccc} R & & R\\ | & & |\\ O & -H\cdots & O-H\end{array}$$

Alchol



$$\begin{array}{ccc} R & & H\\ | & & |\\ H & \cdots\cdots & O-H\end{array}$$

Alcohol and water

Thus we may define hydrogen bond as the weak electrostatic bond which binds hydrogen of one molecule with a highly electronegative element (F, O, N) of another molecule.

Hydrogen bromide, HBr. A compound of bromine and hydrogen. A colourless gas, strongly fumes in the air. Formed in the reaction of bromine vapour with hydrogen at a high temperature. Used in the manufacture of bromides, the bromination of organic substances.

Hydrogen chloride, HCl. A colourless gas with a pungent odour, fumes in the air, very soluble in water with the formation of hydrochloric acid. Dry hydrgen chloride does not attack metals whereas hydrochloric acid is highly corrosive. Poisonous in high concentrations. Made by direct combination of chlorine with hydrogen: $H_2+Cl_2 \rightarrow 22HCl$, or by exchange reaction: $2NaCl+H_2SO_4 \rightarrow 2HCl+Na_2SO_4$. The chief use is hydrochloric acid manufacture.

Hydrogen fluoride, HF. A colourless gas above 253.5 K, a mobile liquid below that temperature; very soluble in water, forms hydrofluoric acid in aqueous solutions. Poisonous.

Preparation By the reaction $CaF_2+H_2SO_4 \rightarrow 2HF+CaSO_4$.

Uses In the manufature of cryolite, uranium fluoroderivatives, Freons organofluorine compounds, for etching and frosting of glass.

Hydrogen iodide, HI. A colourless suffocating gas, strongly fumes in the air. Its solution in water is called hydriodic acid which is a colourless liquid with a pungent odour, a strong acid. Hydrogen iodide is an effective reducing agent. Used as a reagent in laboratory work and for the preparation of various compounds containing iodine.

Hydrogen peroxide, H_2O_2. A colourless viscous liquid with a metallic taste, miscible with water. Very pure hydrogen peroxide is stable; in the presence of traces of heavy metals and their ions (Cu, Fe, Mn, etc.). Decomposes: $2H_2O_2 \rightarrow 2H_2O + O_2$. Can act as a reducing agent and as an oxidant; oxidizes metal nitrites to metal nitrates, the iodide ion to iodine, splits unsaturated hydrocarbons at the double bonds; reduces gold and silver salts, potassium permanganate in acid media. Concentrated solutions of hydrogen peroxide have a burning action on skin. Used for bleaching of wool, silk, wood pulp, etc. Used in the analytical chemistry, medicine, for the production of foam in the manufacture of various porous materials. Because of its strong oxidizing action used in rocket engineering.

Hydrogen sulphide. It occurs widely in nature as a result of volcano and bacterial action, is a prime source of elemental sulphur and sulphides. H_2S is readily prepared treating iron sulphide with HCl or H_2SO_4, or hydrolysing CaS, BaS or Al_2S_3 H_2S is readily soluble in both acidic and alkaline aqueous solutions. In water, 4.65 volumes dissolve at 273K. In aqueous solution, H_2S is a weak dibasic acid. Since H_2O is neutral, acidic character of H_2S is contrary to that expected on the basis of electronegativity. However, the increasing acidic character of the hydrides of Group VI can be understood in terms of increasing size and hence weaker bond with hydrogen. Thus H—O bond being stronger than H—S bond results in a neutral character of the former.

Hydrohalic acids. Aqueous solution of hydrogen halide is called hydrohalic acid, e.g. hydrogen chloride when dissolved in water is named as hydrochloric acid.

Hydrogen halides are generally prepared by the action of conc. H_2SO_4 on the corresponding halides. HF and HCl can be prepared by this method but HBr and HI are oxidized to the corresponding halogen by conc. H_2SO_4. Hence these halides may be prepared by replacing conc. H_2SO_4 or by the reaction of water on the appropriate phosphorus trihalide which may be generated in situ by the reaction of red phosphorus with Br_2 or I_2.

Since HCl, HBr and HI are monomolecular gases, these are completely dissociated in water. On the other hand, hydrogen fluoride is an associated substance on account of hydrogen bonding. Consequgntly hydrofluoric and is a weak acid. In this case H—F bond is much stronger than H—Cl, H—Br and H—I bonds. The order of acidic strength of the four acids is $HF < HCl < HBr < HI$. This order is just reverse to that expected on the basis of electronegativity considerations. Hydrofluoric acid reacts with silica and hence cannot be stored in glass bottles.

Hydroxides. Hydroxides are compounds in which the hdroxyl group is persent as the hydroxide ion (OH^-).

Hypohalites. The salts of hypohalous acids are known as hypohalites. The thermal stability of these decreases with increase in atomic number, e.g. sodium hypochlorite decomposes in hot solution, sodium hypobromite decomposes at 325 K and sodium hypoidite decomposes even at room temperature as given below:

$$3NaOX \longrightarrow 2NaX + NaXO_3$$

Sodium hypochlorite, NaOCl is an important salt.

Hypophosphoric acid, $H_4P_2O_6$. It is obtained on exposing phosphorus to limited supply of moist air alongwith phosphoric and phosphrous acids. The mixture of acids is treated with lead acctate to get the precipitate of lead hypophoshate. This is decomposed by passing hydrogen sulphide gas to get free acid.

$$Pb_2P_2O_6 + 2H_2S \longrightarrow 2PbS\downarrow + H_4P_2O_6$$

It is a colourless crystalline solid. It has two molecules of water of crystallization.

It is hygroscopic in nature and tetrabasic acid.

It is readily hydrolysed by water.

$$H_4P_2O_6 + H_2O \longrightarrow H_3PO_3 + H_3PO_4$$

It decomposes on heating above its melting point.

$$H_4P_2O_6 \longrightarrow H_3PO_3 + HPO_3$$

Hypophoshorous acid, H_3PO_2. It is prepared by treating barium hypophosphite with calculated quantity of dilute sulphuric acid and filtering off the precipitate of barium sulphate, The solution is evaporated and cooled in a freezing mixture to obtain colourless crystals (m.p. 299.5 K) of the acid.

$$Ba(H_2PO_2)_2 + H_2SO_4 \longrightarrow BaSO_4\downarrow + 2H_3PO_2$$

Indeterminate errors. These errors cannot be predictcd or determined accurately.

I

Indium. (from its indigo blue spectrum) **In.** A Group IIIA element of the 5th period of the Periodic Table of Elements, atomic number 49 atomic mass 114.82, two stable isotopes, ^{113}In (4.33 per cent) and ^{115}In (95.67 per cent). Discovered in 1863 by Reich and Richter in zine blende. The spectrum of indium contains intense blue lines whence its name. Was predicted by D.I Mendeleev. A scattered element.

Properties Silvery white colour, m.p. 429 K. An analogue of gallium, the oxidation state +3; forms In_2O_3 upon heating in the air; dissolves in strong acids.

Recovery Certain lead, zine, and tin ores are recovered for indium whose content there ranges from 0.001 to 0.1 per cent.

Uses Corrosion-resistant coating, low-melting alloys: indium compounds have semiconducting properties.

Inert gas (noble gas, rare gas). Any of Group zero elements of the Periodic Table of Elements, i.e. helium, He; neon; Ne; argon, Ar; krypton, Kr; xenon, Xe; or radon, Rn. In nature, inert gases are formed in various nuclear reactions. Constitute some 1 per cent of the atmosphere. Inert gas atoms have stable outer electron shells, a two-electron (He) or an octet (all the other inert gases) shell. This explains their low reactivites. At present, a number of inert gas compounds have, however, been obtained. These are mostly compounds of krypton and xenon with water, fluorine, oxygen, and organic substances. The name 'inert' is therefore not very accurate. Inert gases are used for filling various lamps, in vacuum systems, in electronics, as inert gas shields in various processes.

Inert pair effect. Elements of sub-groups IVA and VA show variable valence exhibiting two states:

(i) Oxidation number=Group number

(ii) Oxidation number=Group number *minus* two

Loss of electrons from an atom of an element can take place in two ways:

Tin (At. no.=50)	2, 8, 18, 18, 4 ($5s^2$, $5p^2$)
Sb (At. no.=51)	2, 8, 18, 18, 5 ($5s^2$, $5p^2$)

(i) All its s and p electrons may be forming a compound in which its oxidation number equals the Group number; for example, in tin(IV) and antimony(V) compouhds are covalent and not ionic.

(ii) The outermost s electrons are not lost very frequently and the oxidation number is equal to Group number minus two, For example, in thalium(I), tin(II), antimony(III) and bismuth(III) compounds, we have

Tl^+	2, 8, 18, 32, 18, 1	(outer $6s^3$ electrons not lost)
Sn^{2+}	2, 8, 18, 18, 2	(outer $5s^2$ electrons not lost)
Pb^{2+}	2, 8, 18, 32, 18, 2	(outer $6s^2$ electrons not lost)
Sb^{3+}	2, 8, 18, 18, 2	(outer $5s^2$ electrons not lost)
Bi^{3+}	2, 8, 18, 32, 18, 2	(outer $6s^2$ electrons not lost)

The pair of s electrons in these elements is said to have become inert. The inert pair effect is most prominent in heavier elements of a group. For example, thalium (Group IIIA) forms univalent thallous halides which are more stable than the tin halides. Tin(II) exists as a simple ion Sn^{2+} and is a strong reducing agent whereas tin(IV) is covalent. Lead(II) is ionic, stable and more common than lead(IV) which is oxidizing. Arsenic and antimony show a variable valency of 3 and 5 while bismuth is only trivalent.

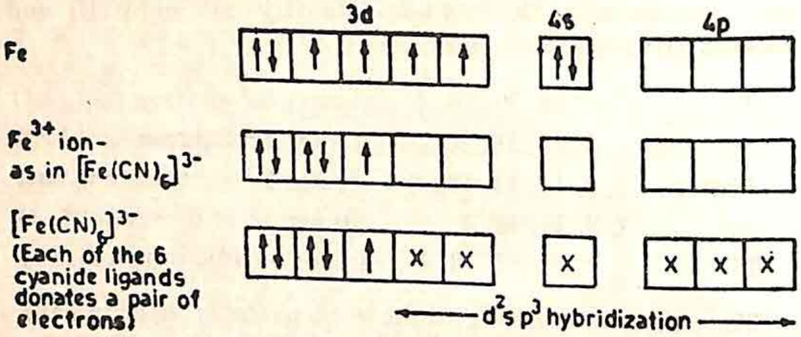
Elements in their lower oxidation states (M^{2+}) are more ionic because of greater radius of M^{2+} than of M^{4+} (smaller the cation, the greater the tendence towards covalency—Fajan's rules).

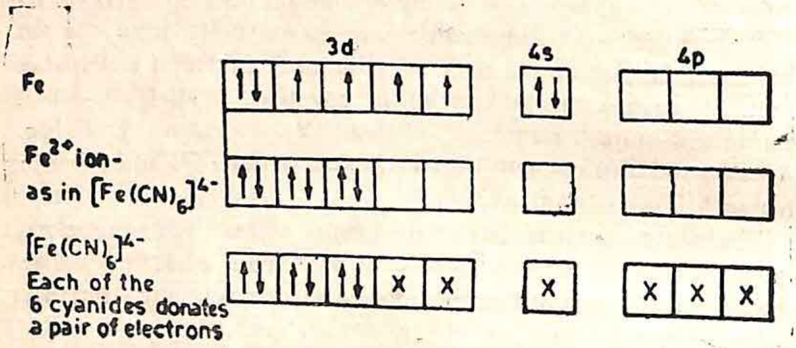
Inner and outer orbital complexes. These are based upon the concept of hybridization. An inner complex is the one in which an 'inner' d, i.e. $(n-1)$d orbital hybridizes along with *n*s and *n*p, orbitals. Inner orbital complexes are formed by strong fields like CN^-, NO_2^-, etc. These complexes are either diamagnetic or have very small magnetic moments.

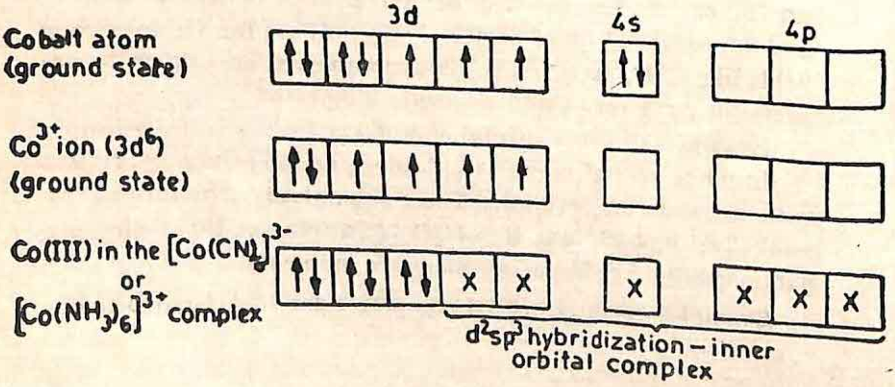
Examples of inner orbital complexes are illustrates below:

In outer orbital complexes, 'outer', i.e. nd orbital hybridizes with us and up orbitals. There complexes are formed by weak field ligands e.g. F^-, H_2O, Cl^-, etc. and are strongly paramagnetic, i.e. large havemagnetic moments.

Examples of outer orbital complexes are illustrated below:

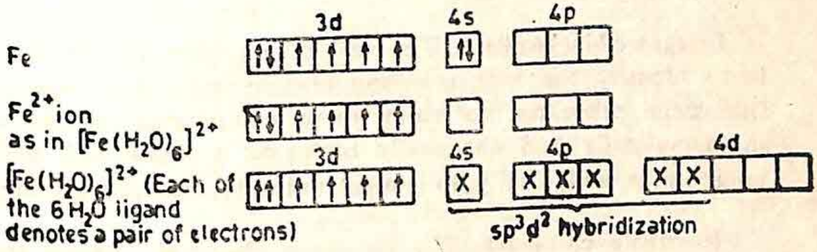

3d
4s
4p
Fe
Fe^{3+} ion-
as in $[Fe(CN)_6]^{3-}$
$[Fe(CN)_6]^{3-}$
(Each of the 6
cyanide ligands
donates a pair of
electrons)
x
d^2sp^3 hybridization

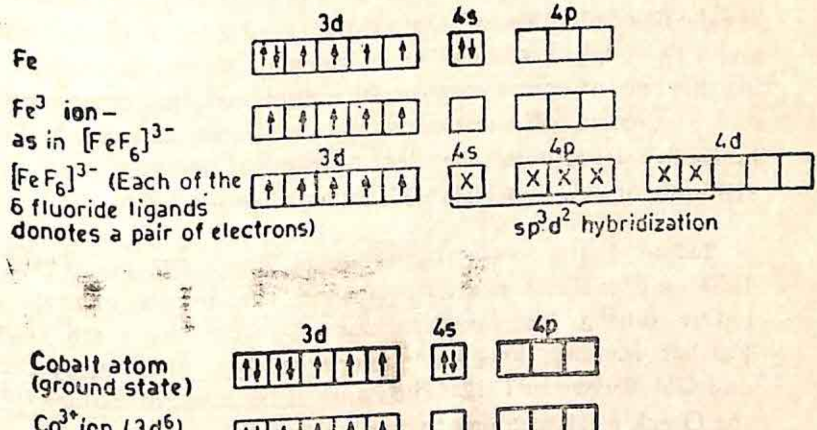

3d
4s
4p
Fe
Fe^{2+} ion-
as in $[Fe(CN)_6]^{4-}$
$[Fe(CN)_6]^{4-}$
Each of the
6 cyanides donates
a pair of electrons
x


3d
4s
4p
Cobalt atom
(ground state)
Co^{3+} ion ($3d^6$)
(ground state)
Co(III) in the $[Co(CN)_6]^{3-}$
or
$[Co(NH_3)_6]^{3+}$ complex
x
d^2sp^3 hybridization – inner
orbital complex

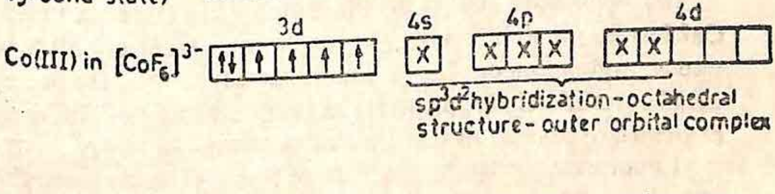
In outer orbital complexes, 'outer', i.e. *n*d orbital hybridizes with *n*s and *n*p orbitals, These complexes are formed by weak field ligands, e.g. F^-, H_2O, Cl^-, etc. and are strongly paramagnetic, i.e. have large magnetic moments.

Examples of outer complexes are illustrated below





3d
4s
4p
Fe
Fe³ ion –
as in [FeF₆]³⁻
3d
4s
4p
4d
[FeF₆]³⁻ (Each of the 6 fluoride ligands donotes a pair of electrons)
X
X X X
X X
sp³d² hybridization



3d
4s
4p
Cobalt atom (ground state)
Co³⁺ ion (3d⁶) (ground state)
3d
4s
4p
4d
Co(III) in [CoF₆]³⁻
X
X X X
X X
sp³d² hybridization - octahedral structure - outer orbital complex

Inner-transition elements. These comprise two series, the lanthanides and actinides. They not only have unfilled d orbitals but also underlying partly filled f orbitals. The regular filling of 4f orbitals in lanthanides and 5f orbitals in actinides accounts for their striking resemblances in most of their properties. Elements within each of these series are very similar in chemical properties because the differentiating electrons are falling in third from the outer shell. They are therefore placed outside the periodic table.

Inorganic biochemistry. The task of inorganic biochemistry is to identify the inorganic compounds involved in various biological processes, to study these compounds, to model mathematically and chemically biological systems with such compounds, and, finally, to control and optimize these systems.

Inorganic chemistry. The science of chemical elements and their compounds (except carbon compounds which are studied under organic chemistry). The inorganic chemistry is based on the periodic law. The major tasks of the inorganic chemistry are the determination of the structure of atoms of elements and a thorough investigation of element properties as depending on their atomic structure, the study of the composition and properties of substances and the determination of their molecular structures, the development of methods for the synthesis of new materials with intended properties.

Iodine. Iodine was discovered by Bernard Courtois (1977-1838), a French chemist. He noticed the purple vapours of iodine during his investigations of ashes from sea weeds. Further investigations were independently carried out by Davy and Gay Lussac in 1812. The name of the element comes from the Greek word meaning "violet coloured."

Iodine occurs only in the combined state as iodides in California oil-well brines, in sea water (traces only), in sea weeds and sponges. Large amounts of iodine are present in caliche (crude Chile saltpetre) as sodium iodate. Traces of the element are present in cod liver oil and human body.

Laboratory preparation of iodine is similar to that of chlorine and bromine. An iodide is heated with manganse dioxide and concentrated sulphuric acid and the vapours are condensed as solid upon the walls of a cold dish or beaker.

$$
\begin{aligned}
&NaI + H_2SO_4 \longrightarrow NaHSO_4 + HI] \times 2 \\
&MnO_2 + H_2SO_4 \longrightarrow MnSO_4 + H_2O + O \\
&2HI + O \longrightarrow I_2 + H_2O \\
\hline
&2NaI + MnO_2 + 3H_2SO_4 \longrightarrow I_2 + 2NaHSO_4 + MnSO_4 + 2H_2O
\end{aligned}
$$

Commercially, it is obtained from sea weeds or crude Chile saltpetre.

Iodine is largely used:

In the manufacture of iodides (used in medicine and photography), iodoform, iodole (antiseptic) and dyestuffs.

In the form of tincture of iodine and iodex as a disinfecant and analgesic.

Tincture of iodine is prepared by dissolving 10 g each of iodine and potassium iodide in 10 mL of water and making the solution to 300 mL with ractified spirit (if needed for internal use as in the case of goitre) or methylated spirit (if needed for external application).

As a reagent in the laboratory and in volumetric analysis.

Iodine in aqueous solution acts as a mild oxidizing agent. Strong reducing agents like sodium thiosulphate, hydrogen sulphide, sulphurous acid and stannous chloride, etc. react rapidly and completely with iodine even in acidic solution; whereas comparatively weaker reducing agents like arsenites and antimonites react completely only in natural or faintly acidic medium. Estimation of reducing substances by the use of standard iodine solution is called *Iodimetry*.

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$$

The above reaction may indirectly be used for the estimation of an oxidizing substance which reacts with potassium iodide to set free an equivalent quantity of iodine, e.g.

$$
\begin{aligned}
&2Cu^{2+} + 4I^- \longrightarrow 2CuI + I_3 \\
&I_3 + 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2I^-
\end{aligned}
$$

All such indirect estimations of oxidizing agents involving the liberation of iodine and subsequent volumetric estimations of the latter are referred to as *Iodometry*.

Iodine heptafluoride, IF_7. It is prepared by the action of flouride on iodine pentafluoridc at 675 K.

$$IF_5+F_2 \longrightarrow IF_7$$

It is a colourless gas and reacts vigorously with non-metals. It is decomposed by water.

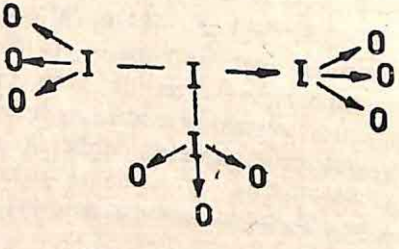
Iodine iodate, $I_4O_9,(IO_3)_3$. It is prepared by heating iodic acid with concentrated phosphoric acid. It is a yellow hygroscopic solid. It absorbs water to form iodine and iodic acid.

$$5I_4O_9+9H_2O \longrightarrow 18HIO_3+I_2$$

It decomposes to from iodine pentoxide and iodine when heated at 395 K.

$$4I_4O_9 \longrightarrow 6I_2O_5+2I_2+3O_2$$

Its structure is given below:



Iodine pentafluoride, IF_5. It is prepared by the action of iodine on fluorine or silver fluoride.

$$I_2+5F_2 \longrightarrow 2IF_5$$
$$I_2+10AgF \dashrightarrow 2IF_2+10Ag$$

It is alsa obtained by the action of flourine on iodine pentoxide.

$$2I_2O_5+10F_2 \longrightarrow 4IF_5+5O_2$$

It is a colourless liquid (b.p. 371K). On passing electric current it ionizes as:

$$2IF_5 \rightleftharpoons IF_4^+ + IF_6^-$$

It forms complex salts with alkali halides.

$$KF + IF_5 \longrightarrow K[IF_6]$$

Iodine pentoxide, I_2O_5. It is prepared by the dehydration of iodic acid or by the oxidation of iodine with concentrated nitric acid.

$$2HIO_3 \xrightarrow{475\text{-}515\ K} I_2O_5 + H_2O$$

It is a white crystalline solid, stable upto 575 K. It dissolves in water to form iodic acid.

$$I_2O_5 + H_2O \longrightarrow 2HIO_3$$

Iodine trichloride, ICl_3. It is prepared by the action of excess of chlorine on iodine or iodine monochloride at 373 K.

$$I_2 + 3Cl_2 \longrightarrow 2ICl_3$$
$$ICl + Cl_2 \longrightarrow ICl_3$$

It can also be prepared by the action of iodine pentoxide on hydrochloric acid.

$$I_2O_5 + 10HCl \longrightarrow 2ICl_3 + 2Cl_2 + 5H_2O$$

It is a yellow crystalline, hygroscopic solid with pungent smell. It dissociates at 341 K as:

$$ICl_3 \longrightarrow ICl + Cl_2$$

It is used in medicines.

Iodimetry. Iodine in aqueous solution acts as a mild oxidizing agent. Strong reducing agents like sodium thiosulphate, hydrogen sulphide, sulphurous acid and stannous chloride, etc. react rapidly and completely with iodine even in acidic solution; whereas comparatively weaker reducing agents such as arsenites and antimonites react completely only in neutral or faintly acidic medium. Estimation of reducing substances by the use of standard iodine solution is called Iodimetry.

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$$

Iodometry. The reaction $2S_2O_3^{2-}+I_2 \longrightarrow S_4O_6^{2-}+2I^-$ may indirectly be used for the esimation of an oxidizing substance which reacts with potassium iodide to set free an equivalent quantity of, iodine, e.g.

$$2Cu^{2+}+4I^- \rightarrow 2CuI+I_2$$
$$I_2+2S_2O_3^{2-} \rightarrow S_4O_6^{2-}+2I^-$$

All such indirect estimations of oxidizing agents involving the liberation of iodide and subsequent volumetric estimations of the latter are called Iodometry.

Interstitial compounds. Interstitial compounds are compounds of indefinite structure and composition. These are formed by the incorporation of small non-metal atoms in the spaces between the metal atoms, i.e. the interstices of the lattice.

Transition metals form intersititial compounds particularly with the small non-metallic atoms hydrogen, boron, carbon and nitrogen. The atoms enter into the vacant holes (interstitial sites) between the packed atoms of the crystalline metal. Interstitial compounds have variable composition, i.e. they are non-stoichiometric. For examples. $TiH_{1.7}$, $VH_{0.56}$, etc.

Interstitial compounds of transition metals, viz. hydrides borides, carbides and nitrides are usually prepared by heating the metal with hydrogen, boron, carbon (or hydrocarbon), and nitrogen (or ammonia), respectively.

Interstitial compounds have the properties of alloys. They are extremely hard, possess good electrical conductivity and are high melting). Except towards strong oxidizing agents, the compounds are inert chemically.

Ionic bond. When a complete transfer of one or more electrons from the valence shell of one atom to the valence shell of the other takes place, both the atoms change into charged species (ions) carrying opposite charges acquiring the electronic configuration of the nearest noble gas. The atom that loses the electron (or electrons) becomes a positive ion and the atom that gains the electron (or electrons) becomes a negative ion. Thus, the two atoms becomes oppositely charged ions and the electrostatic forces of attraction come into play between them tending to lower the potential energy of the system resulting in the formation of a bond between the two atoms. Such a bond is called an ionic bond or electrovalent linkage.

Ionic carbides. The simple compounds of carbon with more electropositive elements, i.e. with the metals of I, II and III groups are known as ionic carbides. These carbides can be prepared by strong heating of metal, its oxide or hydroxide with carbon, carbon monoxide or aceytlene, etc,

$$2Be+C \longrightarrow Be_2C$$
$$2B_2O_3+7C \longrightarrow B_4C+6CO$$
$$4Al+3C \longrightarrow Al_4C_3$$
$$CaO+3C \longrightarrow CaC_2+CO$$
$$2Al_2O_3+9C \longrightarrow Al_4C_3+6CO$$
$$Ag_2O+C_2H_2 \longrightarrow Ag_2C_2+H_2O$$
$$2Li+2CO \longrightarrow Li_2C_2+O_2$$
$$4Li+C_2H_2 \longrightarrow Li_2C_2+2LiH$$

These carbides are transparent solids and bad conductor of electricity. They are easily decomposed by water or acids to form aliphatic hydrocarbons. These carbides are further classified as:

Acetylidcs These contain the carbide ion $(C—COC—)^{2-}$ and yield acetylene on hydrolysis.

$$CaC_2+2H_2O \longrightarrow Ca(OH)_2+C$$

Methanides These contain the C^{4-} ions and yield methane on hydrolysis, e.g. Be_2C and Al_4C_3.

$$Be_2C+4H_2O \longrightarrow 2Be(OH)_2+CH_4$$
$$Al_4C_3+12H_2O \longrightarrow 4Al(OH)_3+3CH_4$$

Allylides These contain the $C_3{}^{4-}$ ions and yield allylene (methyl acetylene, $CH{\equiv}C—CH_3$) on hydrolysis, e.g, Mg_3C_3.

$$Mg_2C_3+4H_2O \longrightarrow 2Mg(OH)_2+C_3H_4$$

Some carbides yield a mixture of several hydrocarbons on hydrolysis such as the carbide of thorium, uranium, lanthanides, etc. They are more closely related to interstitial carbides in structure.

Ionic halides. Halides of alkali and alkaline earth metals (metals having relatively low ionization energy) are ionic in nature. Some of the transition metals in their lower oxidation states, e.g. Fe^{2+} and Mn^{2+} also form essentially ionic halides. Due to their high lattice energies, almost all metallic fluorides are ionic substances.

The ionic halides may be prepared by treating the metal, metal oxide or carbonate with the corresponding halogen acid. These are generally solids having high boiling points. They are good conductors in the fused state and do not undergo extensive hydrolysis. Most of the ionic fluorides especially those having smaller polyvalent metal ions, e.g. MgF_2 and CaF_2, are sparingly soluble in water, a feature related to their high lattice energies. Most of the ionic chlorides, bromides and iodides are soluble in water.

Ionic radius. In an ionic solid each ion, positive or negative has got its influence in the ionic bond formation. The ionic radius of an ion is the effective distance from the nucleus of an atom upto which it has its influence in the ionic bond. Ionic radii have additive character. That is the internuclear distance between two ions is the sum of the two individual radii. For example, the sum of the radii of the ions Na^+ and F^- in sodium fluoride is 2.31 Å. The infiuence of the respective ion on the distance will be inversly proportional to its effective nuclear charge. The effective nuclear charges of Na^+ and F^- ions are 6.5 and 4.5 respectively, their influence on the internuclear distance (2.31) will be in the reverse direction, i.e.

$$\frac{r(Na^+)}{r(F^-)}=\frac{4.5}{6.5}$$

The radii of Na^+ and F^- ions in the distance 2.31 Å will be in ratio of 4.5: 6.5, i.e. 0.95 Å (for Na^+) and 1.36 Å (for F^-).

Ionization energy. The amount of energy required to remove the mest loosely bound electron from a neutral gaseous positive ion is termed as ionization energy or strictly the first ionization energy (E_1). The process may be represented as follows:
Atom (g)+energy→Positive ion (g)+electron

Ionization enerey is also known as ionization potential, because it is amount of potential (or voltage) which is required to dislodge the loosely bound electron from the gaseous atom of the element giving rise to a positive gaseous ion.

The energy required to remove the second electron from monopositive ion is known as the second ionization energy (E_2) the energy required to remove the third electron from a dipositive ion is the third ionization energy (E_3) and so on. That is

$$M^+(g)+E_2 \longrightarrow M^{2+}(g)+e^- \text{ (second ionization)}$$
$$M^{2+}(g)+E_3 \longrightarrow M^{3+}(g)+e^- \text{ (third ionization)}$$

Any unit of energy can be used for ionization energy. Normally it is expressed in kilojoules (kJ) per mole. Electron volt (eV) and kilocalories (kcal) may also be used to express the ionization energy.

Ionization isomerism. The coordination compounds which have the same empirical formulae but produce different ions in soultion are called ionization isomers. For example,

$[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$
(violet) (red)

Violet coloured bromopentaaminecobalt(III) sulphate and red coloured sulphatopentamminecobalt(III) bromide have the same empirical formule but the former gives $[Co(NH_3)_5\,Br]^{2+}$ and SO_4^{2-} ions in solution while the latter gives $[Co(NH_3)_5SO_4]^+$ and Br^- ions in solution. They are, thus, ionization isomers. Similarly,

$[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$
$[Pt(Co(en)_2(NO_2)Cl]SCN$ and $[Co(en)_2(NO_2)SCN]Cl$

are some other examples of ionization isomerism.

Iridium [Greek *iris*, rainbow] **Ir**. A Group VIII element of the 6th period of the Periodic Table of Elements, atomic number

77, atomic mass 192.2, belongs to the platinum family. Disco vered by Tennant in 1804.

Properties silvery white metal, very hard and brittle. Insoluble in acids and aqua regia, stable to chemical actions; the oxidation states are usually +3, +4; forms various complex compounds such as $(NH_4)_2[IrCl_6]$. Iridium derives its name from the colours of its salts which may be green, red, and voilet.

Occurrenc Rarely found in the free state, more frequently as iridosmine, etc.

Uses As a catalyst in the organic synthesis; alloys with platinum are used for electric contacts, thermocouples, for tipping various instruments, in watchmaking, in the manufacture of physical, chemical, medical (surgical) equipment, etc.

Iron [Anglo-Saxon name, Latin *ferrum*, iron] Fe. A Group VIII element of the 4th period of the Periodic Table of Elements, atomic number 26, atomic mass 55.847. Known from the earliest times: iron tools and weapons have been used from 800-600 B.C. (the Iron Age); the introduction and development of metallurgy dates from the same period.

Properties A silvery white ductile metal, very malleable. Moderately active, the oxidation states in compounds +2, +3; heating of iron in the air results in the formation of protective oxide film; in moist air undergoes oxidation and gets covered by rust. Iron easily dissolves in dilute acids, but concentrated acids make it passive (chemically unreactive). Iron reacts with most elements.

Occurrence One of the most abundant elements, occurs in the free state and in ores.

Iron vitriol (ferrous sulphate) $FeSO_4.7H_2O$. Greenish crystals, used in the textile industry, in agriculture (as insecticide), in the manufacture of mineral paints. Forms double salts with alkali metal and ammonium sulphates, e.g. $(NH_4)_2 SO_4.FeSO_4.6H_2O$ known as Mohr's salt and used in the analytical chemistry.

Isobar [Iso+Greek *baros*, weight]. Any of two or more atoms having the same weight but different nuclear charges (atomic numbers) and chemical properties. Isobars represent different chemical elements, e.g. ^{40}Ar, ^{40}K, and ^{40}Ca; ^{54}Cr and ^{54}Fe; ^{112}Cd and ^{112}Sn, etc.

Isoelectronic. Two ions are said to be isoelectronic if they have identical electronic configurations. Examples: Na^+ and Mg^{2+} are isoelectronic.

Isomers. These are compounds having same molecular formula but different structural formula.

Coordination compounds show following types of isomerism.

Stereo isomerism or space isomerism When the isomers of coordination compounds differ in the arrangement of ligands in the space, they are said to be stero-isomers and the type of isomerism is known stero-isomersim or space isomerism. This is also of two types:

(i) Geometrioal (also called cis-trans or position isomerism)
(ii) Optical (also called mirror-image isomerism).

Structural isomerism This is of following types:

(i) Ionization isomerism.
(ii) Hydrate isomerism,
(iii) Linkage isomerism and
(iv) Coordination isomerism.

Isopoly acids. The commonest of the isopolyacids are the parent acids of the paramolybdates, $H_6[Mo_7O_{24}]$, and of the paratungstates, $H_5[HW_6O_{21}]$. Isopolymolybdates and tungstates are formed by acidifying the alkaline solutions of normal molybdates MoO_4^{2-} or tungstates, WO_4^{2-}; the latter ions actually undergo condensation to form polyanions. The extent of polymerization increases as the pH of the solution is lowered.

$$\begin{tikzcd}
MoO_4^{2-} \arrow[r, phantom, "\overset{pH\ 6.5}{\rightleftharpoons}"] & Mo_3O_{11}^{4-} \arrow[r, phantom, "\overset{4.5}{\rightleftharpoons}"] & HMo_6O_{21}^{5-} \arrow[r, phantom, "\overset{9.9-1.5}{\rightleftharpoons}"] & H_3Mo_6O_{21}^{3-} \arrow[d, phantom, "\upharpoonleft\downharpoonright"] \\
& MoO_3.\ aq. \arrow[r, phantom, "\overset{\sim 1.0}{\rightleftharpoons}"] & H_7Mo_2O_{78}^{5-} \arrow[r, phantom, "\rightleftharpoons"] & H_7Mo_{12}O_{44}
\end{tikzcd}$$

At low pH (~1.0) hydrated molybdenum trioxide, $MoO_3.nH_2O$ is precipitated. Similar studies have been done on tungstate and vanadate systems with analogous results.

The structure of the $(Mo_7O_{24})^{4-}$ ion is similar to that of 6-acid anions but with a central, octahedrally co-ordinated Mo atom. Octamolybdates, have also 6-acid anion like structure but with two additional octahedrally co-ordinated molybdenum atoms.

Isotope effect. An isotope effect is a difference in properties between two elements or compounds containing different isotopes of an element. Years ago it was thought that isotopes could have no effect on chemical characteristics such as rate and equilibrium properties. It is known today that such is not the case. The isotope effect, never very large, is most appreciable in compounds of hydrogen, where the percentage difference between the masses of the isotopes is very large.

IUPAC nomenclature of coordination compounds. Coordination compounds are named according to the following IUPAC rules:

While naming an ionic compound cation is named first, and then the anion, which is in accordance with the usual nomenclature rules applied to ionic salts.

NaCl (salt)	Sodium chloride
$[Cu(NH_3)_4SO_4$	Tetraamminecopper(II) sulphate
$[Co(NH_3)_6]Cl_3$	Hexaamminecobalt(III) chloride

(ii) One word name is given to non-ionic or molecular complexes.

$[Pt(NH_3)_2Cl_4]$	Tetrachlorodiammineplatinum(IV)
$[Ir(NH_3]_3Cl_2]$	Trichlorotriammineiridium(III)

(iii) While naming the coordination sphere, whether it is a cation or an anion or a neutral molecule, ligands are named before the central metallic ion.

Thus, $[Co(NH_3)_6]Br_3$ is named as hexaamminecobalt(III) bromide and not as cobalt(III) hexaammine bromide.

(iv) Negative ligands end in suffix—o and positively charged ligands end in the suffix—ium.

Negative ligands		*Positive ligands*	
CN^-	cyano		
Cl^-	chloro	$C_6H_6N^+$	pyidinium
Br^-	bromo	NO^+	nitrosonium

Neutral ligands have their regular names

CH_3NH_2	methylamine
$(C_2H_5)_3N$	triethylamine
$(CH_3)_3P$	trimethylphosphine
$NH_2CH_2CH_2NH_2$	ethylenediamine

There are four important exceptions:

CO	carbonyl;	NO	nitrosyl
NH_3	ammine;	H_2O	aquo

(v) If many ligands are present in a complex, they are named in the following order: Firstly the negative ligands, than the neutral ligands and finally the positive ligands. The names of the ligands are written without any separation by hyphens.

$[Co(NH_3)(NO_2)_3]$ Trinitrotriamminecobalt(III)

If more than one negative or positive ligands are present, then these are named in the order of their increasing complexity.

$[Pt(NH_3)_4(NO_2)Cl]CO_3$ Chloronitroterammineplatinum (IV) carbonate

In a modified version of the above rule it is now recommended that the ligands should be named in alphabetical order regardless of their charge or complexity thus ammine should be listed before chloro.

$[Mn(NH_3)_4Cl_2]NO_3$	Tetraamminedichloromanganese(III) nitrate.

(vi) When more than one simple ligand of a particular kind are present, prefixes di, tri, tetra, penta and hexa are used for 2, 3, 4, 5 and 6 ligands respectively before their names.

$[Cr(H_2O)_4Cl_2]NO_3$ Dichlorotetraaquochromium(III) nitrate

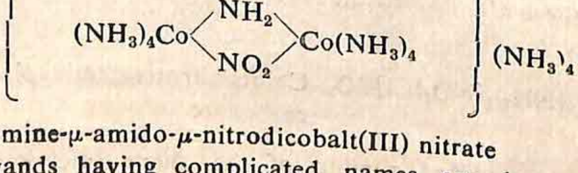
Prefixes bis, tris, tetrakis, pentakis and hexakis are used before the names of 2, 3, 4, 5 and 6 numbers of complex ligands respectively.

$[Ni(dmg)_2$	Bis(dimethylglyoximato) nickel(II)
$[Cr(en)_3]Cl_3$	Tris(ethylenediamine)chromium(III) chloride
$[Co(en)_2Cl_2]Cl$	Dichlorobis(ethylenediamine)cobalt(III) chloride

(vii) For neutral, cationic and nonionic complexes the name of the metal is given as such. For anionic complexes, the name of the metal ends in —ate. The oxidation number of the metal is given by a Roman numeral in parentheses after the name of the metal.

$[Ag(NH_3)_2]Cl$	Diamminesilver(I) chloride
$K[BF_4]$	Potassium tetrafluoroborate(III)
$Na_3[AlF_6]$	Sodium hexafluoroalumintate(II)

(viii) Ligands acting as bridge between two central metallic ions are indicated by the Greek letter, μ proceeding their names. The letter μ is repeated before the name of each different kinds of bridging group.



$$\left[(NH_3)_4Co\begin{smallmatrix}NH_2\\ \\NO_2\end{smallmatrix}Co(NH_3)_4\right](NH_3)_4$$

Octaammine-μ-amido-μ-nitrodicobalt(III) nitrate

(ix) Ligands having complicated names are denoted by abbreviations.

For example,

ethylendiamine is denoted	by	en
1,10-phenenthroline	by	phen
acetylacetonato	by	acac
dimethylglyoxime	by	dmg

J

Javelle water [French *eau de Javelle*, from the place where it was originally produced]. A solution of salt of hydrochloric and hypochlorous acids (KClO+KCl). Used for bleaching. Potassium hypochlorite readily decomposes under the action of atmospheric CO_2 with the formation of hypochlorous acid which has a decolourizing action:

$$KClO + CO_2 + H_2O \rightarrow KHCO_3 + HClO$$

Jeweller's rouge. Iron(III) oxide (Fe_2O_3), used as a mild abrasive.

K

Kainite [Greek *kainos*, new]. A mineral, a double salt of magnesium and potassium, $KCl.MgSO_4.3H_2O$. Colour grey, yellow, or red. Used in the manufacture of potassium fertilizers magnesium metal.

Kipp's apparatus. It is an apparatus for the production of a gas from the reaction of a liquid on a solid. It consists of three globes being connected via a wide tube to the lower globe.

The upper globe is the liquid reservoir. The middle globe contains the solid and also has a tap at which the gas may be drawn off. When the gas is drawn off the liquid rises from the lower globe to enter the middle globe and reacts with the solid. thereby releasing more gas. When turned off the gas released forces the liquid back down inlo the lower globe and up into the reservoir, thus stoppidg the reaction.

Krypton [Greek *kryptein*, to hide] **Kr**. A Zero Group element of the 4th period of the Periodic Table of Elements, atomic number 36, atomic mass 83.80, an inert gas. Isolated from the air in 1898 by Ramsay and Travers. Krypton compounds with fluorine (KrF_4), phenol, chloroform, etc. have been obtained. In industry, it is obtained from the air; used for filling incandescent lamps, electric luminescent tubes (gives white glow) The ^{85}Kr isotope is used as a tracer.

Kurchatovium (after Russian physicist Kurchatov) **Ku**. A Group IV radioactive element of the 7th period of the Periodic Table of Elements, atomic number 104. Synthesized in 1964 by Flerov and co-workers (Dubna, USSR); chemically identified in 1966. Has isotopes with the mass numbers 257, 259, 260 and 261. Resembles hafnium in its chemical properties.

L

Lanthanide contraction. It is regular decrease in the size of atoms/ions with increase in atomic number as we move across from La to Lu. In this series La has the largest radius and Lu has the smallest radius. This decrease in size is known as the lanthanide contraction.

The reason of lanthanide contraction is the imperfect shielding of one 4f electron by another in the same subshell. As we move along the lanthanide series, the nuclear charge and the number of 4f electrons increases by one unit at each step but due to the imperfect shielding (because the shape of f orbitals is such that they are very much diffsued), the Z_{eff} increases causing a contraction in electron cloud of the 4f subshell. For example, in going from La^{3+} to Lu^{3+}, the ionic radii change from 106 pm, to 85 pm in steps averaging about 1.5 pm. The lanthanide contraction plays a significant role in the chemistry of lanthanides. Some important consequences of lanthanide contraction are:

There is a steady decrease in the ionic size.

There is a slight increase in the electronegativity of the trivalent ions.

There is a very small but smooth increase in standard electrode potential values, E^0, for the process

$$M^{3+} + 3e^- \longrightarrow M(g)$$

for lanthanum (La) from —2.52V to —2.25V for lutetium (Lu).

Lanthanides. They form a series of the elements (atomic numbers 58 to 71) following lanthanum (atomic number 57). The elements are: Ce, Pr, Nd, Pm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu. They are also called lanthanons.

Ground state configurations of lanthanides

Element	Symbol	Atomic number	Electronic configuration
Lanthanum	La	57	$4f^0\ 5d^1\ 5s^2$
Cerium	Ce	58	$4f^1\ 5d^1\ 6s^2$ (or $4f^2\ 5d^0\ 6s^2$)
Praseodymium	Pr	59	$4f^3\ 6s^2$
Neodymium	Nd	60	$4f^4\ 6s^2$
Promethium	Pm	61	$5f^5\ 6s^2$
Samarium	Sm	62	$5f^6\ 6s^2$

Europium	Eu	63	$4f^7\ 6s^2$
Gadolinium	Gd	64	$4f^7\ 5d^1\ 6s^2$
Terbium	Tb	65	$4f^9\ 6s^2$ (or $4f^8\ 5d^1\ 6s^2$)
Dysprosium	Dy	66	$4f^{10}\ 6s^2$
Holmium	Ho	67	$4f^{11}\ 6s^2$
Eribium	Er	68	$4f^{12}\ 6s^2$
Thulium	Tm	69	$4f^{13}\ 6s^2$
Ytterbium	Yb	70	$4\ f^{14}6s^2$
Lutetium	Lu	71	$4f^{14}\ 5d^1\ 6s^2$

Separation of lanthanides All lanthanide ions are typically trivalent and almost identical in size. Their chemical properties which are determined by the size and charge of their ions, are almost identical. This renders the separation of one metal from another very difficult. Different methods uscd for their separation are based on the slight differences in their solubility, stability and basic properties.

Lanthanons. Same as lanthanides.

Lanthanum [Greek *lanthano*, to lie hidden] **La.** A Group III element of the 6th period of the Periodic Table of Elements, atomic number 57, atomic mass 138.91. Dsicovered by Mosander in 1839 in the from of lanthanum oxide.

Properties A ductile and malleable metal. Decomposes water at room temperature, readily dissolxes in dilute acids; the oxidation state in componnds+3.

Occurrence Found in monazite, a mineral of a complex composition.

Lapis lazuli (lazulite). A silicate mineral, brittle, colour deep blue to greenish blue. Dissolves in HCl with evolution of

H_2S. Used as a rare beautiful ornamental stone, a material for vases, caskets, statuettes. Thin plates are used in mosaic for facing columns, mantels, etc.

Lattice energy or Crystal energy. Consider the formation of NaCl crystal from solid sodium and gaseous chlorine. First of all the solid sodium and gaseous chlorine are converted into free atoms which are then converted into the free Na^+ and Cl^- ions. These ions then combine together to form the NaCl crystal. The energy released when the requisite number of positive and negative ions join together from infinite distances to form one mole of the crystal is known as the *Lattice energy* of the crystal. Higher the lattice energy of the resulting ionic crystal, greater will be the ease of its formation.

Lawrencium. A radioactive transuranic element of the actinide series, not found naturally on earth. Several very short-lived isotopes have been synthesized. Symbol Lr; atomic number 103.

Leaching process. This involves the purification of the ore chemically. The powdered ore is treated with a suitable chemical agent which dissolves the ore particles while the impurities remain undissolved and can be removed by filtration.

Lead. In comparison to the most abundant metals in the earth's crust, lead is also a rare metal. The occurrence of lead ore deposits is unexpectedly high and they are widely distributed through the world. The most important ore mineral is galena (PbS, 87 per cent Pb).

The natural concetration of lead in soil is in the range of 2-200 mg/kg with mean values of about 16 mg/kg, but the variation from one location to another is considerable. Grass samples may show high lead concentrations near roads with havy traffic, the mean values ranging from about 250 mg/kg at the roadside to about 100 mg/kg at a distance of 25 m.

The mean concentration of lead in rainwater ranges from 8 $\mu g/L$ in residetial areas to about 30 $\mu g/L$ in business areas. In areas of heavy traffic, lead in rain may exceed 100 $\mu g/L$ and reaches 500 $\mu g/L$. However, when lead pipes or tanks are used and the water is soft, lead concentrations may be so high up to 3000 $\mu g/L$ as to cause lead poisoning. Plastic pipes containing lead stearate may also contaminate drinking water. Lead concentration in deep ocean water is about 0.01-0.02 $\mu g/L$, but in surface ocean water 0.3 $\mu g/L$.

The lead concentrations in ambient air range from about 0.02 $\mu g/m^3$ to about 10 $\mu g/m^3$. In contrast, the lead concentrations in air above the north-central pacific oceon and South Indian Ocean are of the order of 0.001 $\mu g/m^3$.

Concentrations of lead in whiskey illicitly distilled using old car radiators may be above 1 mg/L and there are reports of chronic poisoning from this source. Wine is another possible source of lead intake of some people. In some wines the average concentrations ranged from 130 to 190 $\mu g/L$. Lead-based paints represent an important source of excessive lead intake in children. Children may also be exposed to lead from coloured newsprints or lead-painted toys.

Lead content in tobacco may vary from about 3 μg to 12 μg per cigarette of which about 2 per cent is transferred to the main stream smoke. Lead levels in human blood are in the range of 10-20 $\mu g/100$ mL on the average.

Lead is an important startegic metal and finds wide applications both in military and civilian uses, the main consumption of lead is in lead-acid batteries and in cable sheathing. Lead is a useful material for shielding against radiation because of its density and high atomic number. It is widely used in hospitals, laboratories and in nuclear power stations as a barrier to radiation from radioactive materials and for the protection of people. Lead is also used for transport and storage of radioactive substances. Lead is now being considered for disposal of nuclear wastes and containment of radiation. It is likely that in future, use of lead for containment of nuclear waste will considerably increase. Lead is a relatively soft metal. This property of lead is now being exploited for use of lead in antivibration pads and sound insulation matresses for building and machinery. Some of the organic chemicals of lead have been found suitable as antioxidents for oils, rubber and asphaltic materails. The lead compounds are also used as roofing asphalt stabilizers. It is expected that use of lead chemicals in such applications will increase considerably in future.

A major source of error in the determination of lead in environmental samples is the secondary contamination which can occur during sampling or analysis. particularly of food and biological media.

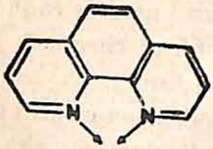
The dithizone method based on spectrophotometric determination of a red complex that lead forms with diphenylthiocarbazone is still widely used although it is being gradually displaced by atomic absorption spectrophotometry (AAS). More recently various flameless AAS procedures have been developed in which the sample is heated and ashed in the receptacle of the AAS instrument. The achievable precision of AAS methods is approximately 7-9%.

Electroanalytical methods are also useful, particularly polarography and anodic stripping voltametry (ASV). Neutron activation analysis is not likely to find wide application for lead analysis in the near future because a fast neutron source is necessary. Another non-destructive method with good potential for specialized applications is X-ray fluorescence. Normal levels of lead in blood (10-20 μ/g100 mL) can be easily determined in a 5 mL sample by AAS, only 0 2 mL is required for ASV; one drop is sufficient for AAS using the Delves cup technique. According to a recent report the dithizone method based on spectrophotometic determination of lead is most sensitive and convenient method from the analyst's point of view.

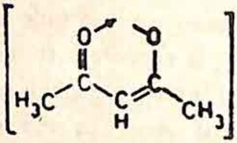
Ligand (or coordinating grup). It is an atom, ion or molecule which can donate a pair electrons to the central metal atom in a complex. The particular atom in a ligand, which actually donates the electron pair is called the donor atom. If a ligand contains only one donor atom it is a uni or monodenate ligand. Examples of some monodentate ligands are:

F^-, Cl^-, Br^-, CN^-, SCN^-, OH^-, H_2O, NO_2, pyridine, etc.

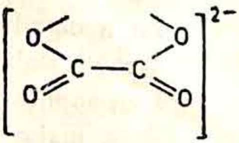
Bidentate ligands



1,10-Phenanthroline
(phen)

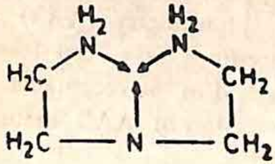


Acetylacetonate ion
(acac)

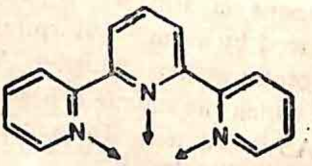


Oxalate ion

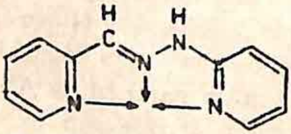
Tri- or terdentate ligands



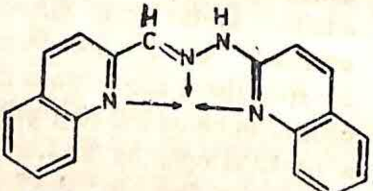
Diethylenetriamine
(dien)



2,2′,2″-Terpyridine
(terpy)

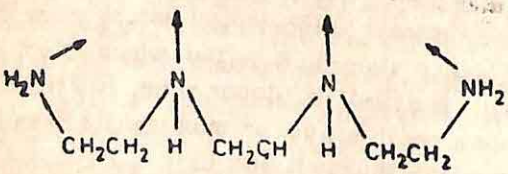


Pyridine-2-Aldehyde-2-
Pyridylhydrazone

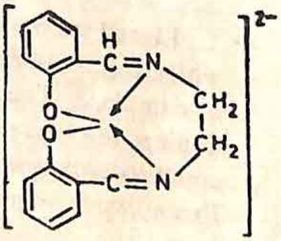


Quinoline-2-Aldehyde-2-
Quinolyhydrazone

Tatra- or quadridentate ligands

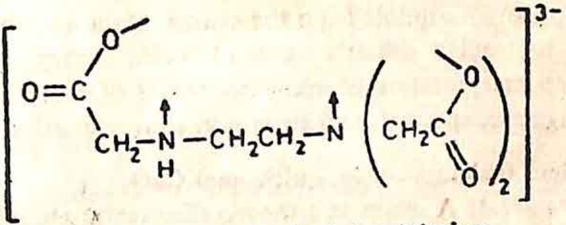


Triethylenetetramine
(trien)



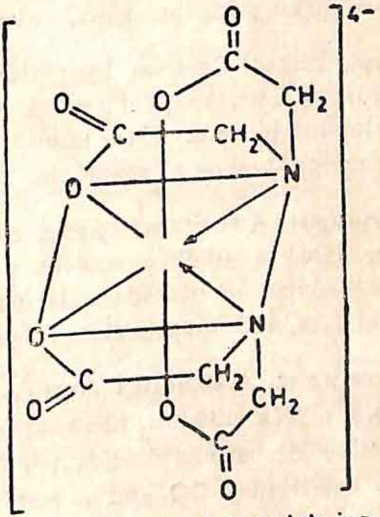
Ethylenebis (salicylaldimine)
ion

Penta- or quinquedentate ligands



Ethylenediaminetriacetate ion

Hexa- or sexadentate ligands



Ethylenediamine tetracetate ion
(edta)

Ligand-field theory. Ligand-field theory goes a step beyond crystal field theory by adding consideration of covalent bonding between the central atom and the ligands. This is done by combining atomic orbitals from the central atom and the ligands to form molecular orbitals. Ligand field theory provides an elegant interpretation of many properties of complex ions such as magnetic, spectral, and structural characteristics.

Lime (calcium oxide, quicklime) **CaO**.

Properties A white substance, effectively absorbs mositure and carbon dioxide:

$$CaO + H_2O \rightarrow Ca(OH)_2$$
$$Ca\,(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

Preporation By roasting limestone or chalk.

$$CaCO_3 \xrightarrow{1175\ K} CaO + CO_2$$

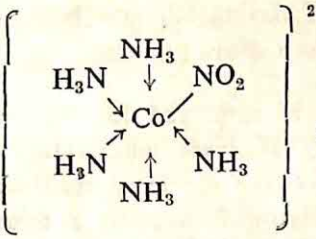
Uses making cement, glass, calcium carbide, slaked lime.

Lime, slaked. Calcium hydroxide, $Ca(OH)_2$. Obtained by the action of water on quicklime. A strong base with a relatively low solubility in water. Used in building, in the chemical industry, in the production of sugar, etc.

Limestone. A sedimentary rock composed mainly of calcite, $CaCO_3$. Used in building, cement production, in metallurgy, in the manufacture of soda, chlorinated lime, calcium carbide, mineral dyes, and in agriculture for liming soil.

Lime water. A saturated aqueous solution of calcium hydroxide, $Ca(OH)_2$, alkaline, turns turbid in the air because of the absorption of carbon dioxide and formation of $CaCO_3$. Used for the detection of CO_2 and in medicine.

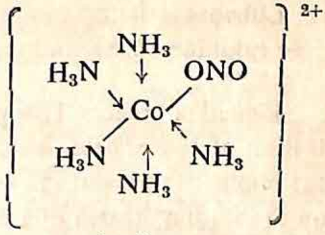
Linkage isomerism. This type of isomerism arises out of two modes of attachment of the ligand to the central metal ion through two different donor atoms. For example, NO_2^- may attach with metal either through O-atom or through N-atom. Similary, SCN^- may be coordinated with the metal either through N- or through S-atom. Thus, we have:



(yellow-brown)

Nitropentaamminecobalt(III) ion

and



(red)

Nitritopentaamminecobalt(III) ion

Liquid fertilizers. Nitrogenous and complex fertilizers used in the liquid state such as liquid ammonia, ammonia water, ammonia complexes, and complex fertilizers containing nitrogen, phosphorus, potassium, and microelements.

Lithium [Greek *lithos*, a stone] **Li.** A Group IA element of the 2nd period of the Periodic Table of Elements, atomic number 3, atomic mass 6.939, discovered by Arfvedson in 1817.

Properties Silvery white colour, the lightest metal. Belongs to alkali metals, the oxidation state in compounds+1. turns tranished in the air because of the formation of the oxide, Li_2O, and nitride, Li_3N; reacts with water less vigorously than the other alkali metals; lithium hydroxide is a strong base. Lithium and its compounds give carmine-red coloration when put into flame.

Occurrence Rather wide-spread, occurs in rocks, mineral springs, sea water, bituminous coal, soil, animal and plant tissues.

Manufacture By the electrolysis of lithium chloride.

Uses An important element for nuclear energy devices, the ${}^{6}_{3}$Li isotope is employed in the preparation of tritium: ${}^{6}_{3}Li+{}^{1}_{0}n\rightarrow$ ${}^{3}_{1}H+{}^{4}_{2}He$; lithium is used as material for control rods in uranium piles and as coolant, in ferrous and nonferrous metallurgy in chemistry (organolithium compounds). Lithium compounds are used in in the manufacture of glass.

Lithopone. It is a miuture of barium sulphate ($BaSO_4$) and zinc sulphide (ZnS), and is used as a white pigment.

Liquation process This process is employed for the concentration of those ores which melt at lower temperature than the impurities present in them. Here the powdered ore is heated on the sloping hearth of a reverberatory furnace at a temperature which is slightly more than its melting point. The melted ore flows away leaving behind impurities.

Lithium carbonate, Li_2CO_3. It can be precipitated by adding ammonium carbonate to a solution of a lithium salt.

$$Li_2SO_4+(NH_4)_2CO_3 \rightarrow Li_2CO_3+(NH_4)_2SO_4$$

On passing carbon dioxine through its suspension in water, it dissolves forming lithium bicarbanate which exists only in solution.

$$Li_2CO_3+H_2O+CO_2 \rightarrow 2LiHCO_3$$

This solution is known as 'lithia water' and is used as remedy for gout. On heating the solution, carbon dioxide is expelled and the carbonate is reprecipitated.

On heating lithium carbonate decomposes to give lithium oxide.

Lutetium It is a silvery element of the lanthanoid series of metals. It occurs in association with other lanthanoids. One of its few uses is as a catalyst.

Symbol: Lu: m.p. 1936 K; b.p. 3668 K.

M

Magnesium. [Geerk *Magnesia lithos*, stone of Magnesia, district in Thessaly] Mg. A Group IIA element of the 3rd period of the Periodic Table of Elements, atomic number 12, atomic mass 24.305. First isolated by Davy in 1808 as magnesium amalgam, prepared in coherent form by Bussy in 1828.

Properties A light silvery white metal, turns tarnished in the air because of oxidation. The oxidation state in compounds +2; very reactive, burns with an intense white light in the air, reacts vigorously with some other elements, slowly replaces hydrogen from water under reflux; does not react with alkalis. Magnesium is a strong reducing agent, at high temperatures reduces metals from their oxides and halides, e.g. alkali metals, beryllium, aluminium, etc.; also reduces nonmetals such as boron and silicon.

Occurrence Various silicate rocks (serpentine, olivine, etc.), magnesite, dolomite, carnallite, etc.; also found in sea water, mineral springs, etc.

Manufacture By the electrolysis of $MgCl_2$ (carnallite).

Uses Magnesium metal is mostly used in the production of light alloys, e g. with aluminium (10%Mg+90% Al); it is also employed to isolate Ti, Zr, V, U, and other metals, in the manufacture of pig iron to increase its strength, in flash bulbs, incendiary bombs, etc. The most important magnesium compounds are magnesium oxide, MgO (magnesia), used in the manufacture of high-temperature crucibles and refractory bricks, in medicine; magnesium sulphate (Epsom salts), $MgSO_4.7H_2O$, contained in sea water, used as a laxtative; magnesium carbonate (magnesite) $MgCO_3$, used in building and in the chemical industry. Magnesium forms many organic derivatives used in various organic syntheses, e.g. Grignard reagents *R*Mg*X*, where *X* is a halogen. A mixture of MgO, $MgCl_2$, and H_2O gives Mg (OH)Cl upon solidification and can be used as a binder. Magnesite and dolomite, $MgCO_3.CaCO_3$. are used in the manufacture of refractories and as fertilizers: magnesium salts are essential to plants because chlorophyll contains magnesium.

Magnesium alloys Magnesium forms tough and light alloys with main metals. Some very important alloys are described below:

Alloy	*Composition*	*Properties*	*Uses*
Magnalium	Mg 80% Al 90%	Lighat and hard	Pistons of gasoline engine, air craft, beames of balances.
Elektron	Mg 95% Zn, Al, Mn, Cu } %5	Do	Do
Dow Metal	Mg 89% Al 9% Zn 2%	Do Tensile as steel	Casting, rolling, die casting and drawing, Making parts of light machines.

Magnesium hydride, MgH_2. It is prepared by the direct reaction of hydrogen on heated magnesium powder.

$$Mg + H_2 \longrightarrow MgH_2$$

It is light grey solid. It evolves hydrogen when heated with water or alone at 555 K.

$$MgH_2 + 2H_2O \longrightarrow Mg(OH)_2 + H_2$$
$$MgH_2 \longrightarrow Mg + H_2$$

It reacts with diborane and aluminium chloride in ether to form magnesium borohydride and aluminohydride.

$$MgH_2 + B_2H_6 \longrightarrow Mg(BH_4)_2$$
$$4MgH_2 + 2AlCl_3 \longrightarrow Mg(AlH_4)_2 + 3MgCl_2$$

Magnesium oxide, MgO. It is prepared by burning magnesium in air.

$$2Mg + O_2 \longrightarrow 2MgO$$

It may be prepared by heating magnesium hydroxide, nitrate, sulphate or carbonate in air.

$$Mg(OH)_2 \longrightarrow MgO + H_2O$$
$$2Mg(NO_3)_2 \longrightarrow 2MgO + 4NO_2 + O_2$$
$$2MgSO_4 \longrightarrow 2MgO + 2SO_2 + O_2$$
$$MgCO_3 \longrightarrow MgO + CO_2$$

The oxide prepared by heating magnesite ($MgCO_3$) is called calcined magnesia.

Magnesium oxide is a light white infusible powder (m.p. 3123 K).

It is sparingly soluble in water. It combines with water to form the hydroxide.

$$MgO+H_2O\longrightarrow Mg(OH)_2$$

It easily reacts with acids.

$$MgO+2HCl\longrightarrow MgCl_2+H_2O$$

It dissolves in aqueous solution of magnesium chloride or bromide to form basic salts such as:

$$MgBr_2.9Mg(OH)_2.5H_2O$$

It also undergoes the following reactions:

$$MgO+C+S\longrightarrow MgS+CO$$
$$2MgO+CS_2\longrightarrow 2MgS+CO_2$$
$$MgO+CaC_2\longrightarrow Mg+CaO+2C$$
$$MgO+CO+Cl_2\longrightarrow MgCl_2+CO_2$$

It is reduced by carbon to form magnesium carhide at high temperature.

$$MgO+3C\longrightarrow MgC_2+CO$$

Some of the uses of magnesium oxide are as follows:

As magnesium oxide is resistant to change at high temperatures, it is used as a refractory material for lining electric furnaces.

In Sorel's cement for plaster casting, repairing porcelain ware and in filling teeth.

In medicines to lower acidity of the stomach.

As an absorbent in the manufacture of dynamite.

As a basic lining in furnaces.

Manganese. Compounds of manganese were known to the ancients. Metallic manganese was obtained by Gahn in 1774 by reduction of the oxide with carbon. A pure sample was, however, obtained by John in 1870. Its name is derived from the Latin *magnes* meaning magnet.

Manganese does not occur free in nature. Its most important ore is pyrolusite MnO_2, large quantities of which are found in India at Panch Mahal (Bombay), Karnataka and Singbhum (Bihar). Other less important minerals are braunite, Mn_2O_3; manganite, $Mn_2O_3.H_2O$, and hausmanite, Mn_3O_4.

Manganese may be extracted from its oxide ores by either of the following two processes:

Carbon-reduction process High grade ores are mixed with charcoal and a little borax and heated to a white heat in an electric furnace when the oxides are reduced to metallic manganese.

$$Mn_3O_4+4C \rightarrow 3Mn+4CO$$
$$MnO_2+2C \rightarrow Mn+2CO$$

Manganese obtained is not pure. However, if less than the theoretical amount of carbon is used, a purer metal nearly free from carbon is obtained.

Aluminothermic process A pure metal is obtained by reducing the oxide, Mn_3O_4 with metallic aluminium (Goldschmidt's aluminothermic process).

$$3Mn_3O_4+8Al \rightarrow 9Mn+4Al_2O_3$$
$$3MnO_2+4Al \rightarrow 3Mn+2Al_2O_3$$

Pure manganese Very pure manganese is obtained by the electrolysis of a solution of manganese chloride using a mercury cathode. Manganese is liberated on the cathode and forms amalgam which is distilled in vacuum to remove mercury.

Uses In the form of ferromanganese (contains 70-80% Mn) and spiegeleisen (contains 15-20% of manganese), it is used in the manufacture of steel. These are used for removing oxygen from the steel and for introducing the desired carbon content in it. Besides this, the presence of manganese in steel makes it more tough. These are produced by reducing a mixture of manganese and iron ore in calculated quantities with carbon in a blast furnace

In the preparation of its alloys.

Manganese steel It contains 9-14 per cent of manganese and is very hard and tough.

Manganese bronze It contains copper (55-65%), zinc (30-45%), iron (0.5-2%) with manganese and aluminium (0.2-4%). It is used in shipping industry. It contains no tin. The name bronze is, therefore, misnomer, It is really manganese brass and not bronze.

Manganin It is an alloy of copper (82-84%), manganese (12-15%), nickel (2-4%) and iron (0-1%). It is employed for making resistance wires.

Manganese compounds. The most important are Mn^{2+} salts, manganese dioxide, MnO_2, and potassium permanganate. Manganous oxide, MnO, is a basic oxide, dissolves in acids to give Mn^{2+} salts, e.g. $MnSO_4$ which is a microfertilizer. MnO is a semiconductor, it is also used in the manufacture of ferrites and paints. $Mn(OH)_2$ is a weak base formed as a white precipitate which turns brown in the air because of oxidation to $Mn(OH)_4$. Manganese dioxide, MnO_2 is an oxidizing agent, used in dry batteries as catalyst. Manganese(VI) derivatives include salts of unstable manganic acid, manganates, e.g. potassium manganate K_2MnO_4; these salts are dark-green substances. Salts of permanganic acid, $HMnO_4$, called permanganates are of greater importance. An example is potassium permanganate, $KMnO_4$, a violet solid, a powerful oxidizing agent. Cyclopentadienyltricarbonylmanganese is the organo-manganese derivative used as an anti-knock agent less toxic than tetraethyllead.

Marsh-Berzillius test. It is most important test for arsenic and is useful for detecting trace amounts of arsenic.

Pure zinc (free from arsenic) and pure dilute sulphuric acid are taken in a flask. Arsenic solution is introduced in the flask through thistle funnel. The exit tube is connected to another tube containing calcium chloride and lead acetate. The nascent hydrogen is produced (Zn/H_2SO_4) which after going through lead acetate and calcium chloride (H_2S and moisture are absorbed) burns as blue flame at the jet without formation of black mirror. The arsenic solution is now dropped through thistle funnel. Nascent hydrogen reacts with arsenic forming arsine which gives black or brown mirror prior to jet.

$$\begin{aligned} Zn+H_2SO_4 &\longrightarrow ZnSO_4+2H \\ AsCl_3+6H &\longrightarrow AsH_3+3HCl \\ 2AsH_3 &\longrightarrow 2As+3H_2 \\ &\qquad\text{(black mirror)} \end{aligned}$$

Mass defect. It is found that the actual masses of atoms of different elements are not the same as obtained by addition of masses of the component paticles. The difference between the calculated mass (M) and the actual mass (A) is known as the mass defect.

Except for hydrcgen-1 the mass of an atom is less than the total mass of the protons, neutrons and electrons composing it. For example, for O-16, the actual atomic mass (A) is 15.99491 amu, but the sum of 8 protons, 8 neutrons and 8 electrons is 16·13192 amu.

Total mass of 8 neutrons $= 8 \times 1{\cdot}008665$ amu

$= 8{\cdot}06932$ amu

Total mass of 8 protons and 8 electrons

$= 8 \times 1{\cdot}007825$ amu

$= 8{\cdot}06260$ amu

Thus total mass (M) of 8 neutrons, 8 protons and 8 electrons comprising $^{16}_{8}O = (8{\cdot}06932 + 8\ 06260)$ amu

$= 16{\cdot}13192$ amu

The difference, i.e. mass defect ($M—A$) is

$= 16{\cdot}13192 — 15\ 99491$ amu

$= 0{\cdot}13701$ amu

Therefore the mass defect for O-16 is 0·13701 amu.

Matter wave. In case of light certain phenomena (photoeletric effect and black body radiation) can be explained if the light is supposed to have particle nature, whereas certain other phenomena can be explained if the light is supposed to have wave nature. Thus light radiation possesses both wave and particle properties. Based on this reasoning de Broglie (1924) suggested that a wave character is associated with a moving particle, such as an electron, a proton, an atom, a molecule or a piece of chalk. The wave associatec with such material particles is called matter wave.

Mean value. It is obtained by dividing the sum of a set of replicate measurements by the number of individual results in the sets.

Median value. It is the value about which all other values in a set are equally distributed. Half the values are higher and the other half smaller numerically, compared to the median value.

Mendelevium. It is a radioactive transuranic element of the actinoid series, not found naturally on earth. Several short-lived isotopes have been synthesized.

Symbol: Md; p.n. 101; stablest isotope ^{258}Md (half-life 60 days).

Mendeleev's periodic table. In March 1869, Mendeleev gave his famous table of periodic classification of elements. He arranged all the elements known at that time in horizontal rows in order of increasing atomic weights. He left some gaps in the table for undiscovered elements and also predicted their properties. Eventually, when these elements were discovered, it was amazing to find that they fitted correctly in the table. For example, as can be seen in Mendeleev's original periodic table (Table), there are two gaps between zinc (Group II) and arsenic (Group V). As these undiscovered elements were to follow aluminium and silicon, Mendeleev named them eka-aluminium and eka-silicon. When these elements, now known as gallium (eka-aluminium) and germanium (eka-silicon), were discovered their properties compared very well with those given by Mendeleev.

TABLE

Based on Mendeleev's Original Periodic Table of 1871

	Group														
Period	I		II		III		IV		V		VI		VII		VIII
	a	b	a	b	a	b	a	b	a	b	a	b	a	b	a
1	H 1.0														
2	Li 6.9		Be 9.0			B 10.8		C 12.0		N 14.0		O 16.0		F 19.0	
3	Na 23.0		Mg 24.3			Al 27.0		Si 28.1		P 31.0		S 32.1		Cl 35.5	

4	K 39.1	Ca 40.1		Ti 47.9	V 50.9	Cr 52.0	Mn 54.9	Fe Co Ni 55.8 58.9 58.7
	Cu 63.5	Zn 65.4			As 74.9	Se 79.0	Br 79.9	
5	Rb 85.5	Si 87.6	Y 88.9	Zi 91.2	Nb 92.9	Mo 95.9		Ru Rh Pd 101.1 102.9 106.4
	Ag 107.9	Cd 112.4	In 114.8	Sn 118.7	Sb 121.8	Te 127.6	I 126.9	
6	Cs 132.9	Ba 137.3	La 138.9		Ta 180.9	W 183.9		Os Ir Pt 190.2 192.2 195.1
	Au 197.0	Hg 200.6	Tl 204.4	Pb 207.2	Bi 209.0			

The above Russian stamp shows Mendeleev predicting the atomic mass of the element that was discovered later in 1875 and named gallium

Mercury. Mercury occurs in the earth's crust mainly in the form of sulphides. It is estimated to occur in continental rocks in a range of 10-1030 ppb. In petroleum it occurs in a range of 2000-20,000 ppb. Mercury is found in all animal tissues at a very low concentration. Some plants appear to concetrate Hg, microdroplets of elemental mercury are sometime found in plant tissues. The human adult body contains about 13 mg Hg, 70 per cent of which is found in fat and muscle tissues and traces in nails and hair. Mercury is found in trace amounts in most foods and water. Ground water contains between 10 and 50 ng Hg/L, while surface water in uncontaminated areas may contain up to 200 ng/L. In rivers draining industrial areas, levels around 1 µg/L may occur. Ocean water contains less mercury, around 30 ng/L.

Large tuna fish exceeding 60 kg have levels up to 1 mg/kg of methylmercury in their muscles, while terrestrial animals rarely have levels in muscles exceeding 50 µg/kg and generally average 20 µg/kg. The mercury concentration in food products excluding fish varies between a few micrograms to 50 µg/kg.

Mercury concentration in the general atmosphere varies from a few ng/m^3 in remote uncontaminated areas up to around 50 ng/m^3 in urbanized areas. Mercury concentrations in atmosphere have been reported high near areas of industrial emission or areas where mercury fungicides are manufactured/used.

Mercury compounds are used in agriculture as fungicides, pesticides, bactericides and disinfectants. Mercury is used as a catalyst for the production of vinyl chloride monomers urethane foams, anthraquinone derivatives and other products. The main use for mercury is in electrial appliances which include batteries, electrical lamps and wiring and switching devices. Mercury is used in many industrial and medical instruments to measure or control reactions and equipment functions, including thermometers, monometers, and other pressure sensing devices. Mercury is used in paints as a fungicide to prevent mildew after the paint has been applied and as a bactericide. Mercury compounds find use in pharmaceuticals as diurectics, antiseptics, skin preparations and preservatives.

In recent years, the number and variety of quantitative or qualitative methodsand instruments used to determine trace quantities of inorganic and organic mercury occurring in natural or synthetic substances have increased greatly. Mercury analysis atconcentrations often found in the environment and in biologicalmaterial (⊲1-2000 μg/kg) is complicated, difficult and requires considerable skill and experience on the part of the analyst. Colorimetric, flameless atomic absorption and neutron activation analysis are the three principal types of methods which have gained general recognition.

Colorimetric method was formerly used extensively, but its not so impressive limit of detection around a few micrograms 0.05 mg/kg in a 0.01 kg sample and its time consuming nature, are major disadvantageous.

Flameless atomic absorption and neutron activation method have replaced the colorimetric methods. The detection limit for atomic absorption is 1-5 ng of Hg. The detection limit for neutron activation is 0.1-0.3 mg Hg in a 0.3 g sample.

Though AAS and neutron activation methods are very convenient from the analyst's point of view but the accessibility of the instrumental facility to a common analyst/chemist is a hurdle in their choicc and one has to look for some alternate method. Spectrophtometric methods then become the methods of choice.

Among all the methods, the extractive spectrophotometric dithizone method has excellent sensitivity and selectivity, and is particularly useful in determining traces of mercury in biological material and food stuffs. Extractive methods using ion-pairs of anionic mercury(II) halide complexes and basic dyes are worthy of mention by virtue of their sensitivity. This method involves extraction of mercury(II) from an acidic medium into chloroform or carbon tetrachloride as orange yellow dithizonate $Hg(HDz)_2$. In deficiency of dithizone and alkaline or neutral solution, violet dithizonate, HgDz, is formed. Though mercury dithizonate is readily formed even in presence of 5 M H_2SO_4, HCl concentration greater than 1 M retards the dithizonate formation owing to the formation of stable mercuric chloride.

Metaphosphoric acid, HPO_3. It is prepared by heating orthophosphoric acid or pyrophosphoric acid.

$$H_3PO_4 \xrightarrow[\text{red}]{875\ K} HPO_3 + H_2O$$

$$H_4P_2O_7 \xrightarrow[\text{heat}]{} 2HPO_3 + H_2O$$

It is also obtained by dissolving phosphorus pentoxide in cold water.

$$P_4O_{10} + 2H_2O \rightarrow 4HPO_3$$

It is a transparent glassy solid (m.p. 311.4 K) and also known as glacial phosphoric acid.

It is soluble in water and its solution changes into orthophosphoric acid on boiling.

$$H_3PO_3 + H_2O \rightarrow H_3PO_4$$

It is a monobasic acid and forms metaphosphates $(NaPO_3)_n$.

It is not a monomer of the formula HPO_3. It is a polymeric acid of the formula $(HPO_3)_n$ where $n=2, 3 \ldots 6$. $(NaPO_3)_3$ is known as calgon used as a water softner.

Modern periodic table. According to the modern periodic law, the properties of the elements and their compounds are a periodic function of their atomic numbers. Thus, in the modern periodic table. atomic number (which is equal to the nuclear charge) forms the basis of the classification of elements.

There are several forms of the periodic table. The most popular version is the long form (Table). In the table, there are seven horizontal rows called *periods*. Each period starts with a new principal quantum number, *n*. and the electrons are filled up in orbitals according to the aufbau princlple. The first period has two elements, hydrogen ($1s^1$) and helium ($1s^2$), and the first shell (K) is completed. The second period starts with $n=2$, and has eight elements. Starting with lithium ($2s^1$), it ends with neon ($2s^2\ 2p^6$) and thus completes the second shell (L). The third period shell M ($n=3$) also contains eight elements. It starts with sodium ($3s^1$) and completes at argon ($3s^2\ 3p^6$).

$${}_{11}\mathrm{Na}[1s^2 2s^2 2p^6]3s^1 \quad \underset{3s}{\uparrow} \quad \underset{3p}{\_\ \_\ \_} \quad \underset{3d}{\_\ \_\ \_\ \_\ \_}$$

$${}_{18}\mathrm{Ar}[1s^2 2s^2 2p^6]3s^2\ 3p^6 \quad \underset{3s}{\uparrow\downarrow} \quad \underset{3p}{\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow} \quad \underset{3d}{\_\ \_\ \_\ \_\ \_}$$

In contrast to the sceond period, the outer shell is not completely filled in elements of the third period and the orbitals of the 3d subshell remain vacant. Element in which the s-subshell is filled are called s-block elements and those in which the p-subshell is filled are known are p-block elements. The fourth period, the N shell ($n=4$) starts filling with potassium

Representative elements (s-block elements)

Transition elements (d-block elements)

Representative elements (p-block elements)

Noble gases

Group number

Period number	Group 1.	Group 2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	Group 18
1	1 H $1s^1$																	2 He $1s^2$
2	3 Li $2s^1$	4 Be $2s^2$											5 B $2s^2 2p^1$	6 C $2s^2 2p^2$	7 N $2s^2 2p^3$	8 O $2s^2 2p^4$	9 F $2s^2 2p^5$	10 Ne $2s^2 2p^6$
3	11 Na $3s^1$	12 Mg $3s^2$											13 Al $3s^2 3p^1$	14 Si $3s^2 3p^2$	15 P $3s^2 3p^3$	16 S $3s^2 3p^4$	17 Cl $3s^2 3p^5$	18 Ar $3s^2 3p^6$
4	19 K $4s^1$	20 Ca $4s^2$	21 Sc $3d^1 4s^2$	22 Ti $3d^2 4s^2$	23 V $3d^3 4s^2$	24 Cr $3d^5 4s^1$	25 Mn $3d^5 4s^2$	26 Fe $3d^6 4s^2$	27 Co $3d^7 4s^2$	28 Ni $3d^8 4s^2$	29 Cu $3d^{10} 4s^1$	30 Zn $3d^{10} 4s^2$	31 Ga $4s^2 4p^1$	32 Ge $4s^2 4p^2$	33 As $4s^2 4p^3$	34 Se $4s^2 4p^4$	35 Br $4s^2 4p^5$	36 Kr $4s^2 4p^6$
5	37 Rb $5s^1$	38 Sr $5s^2$	39 Y $4d^1 5s^2$	40 Zr $4d^2 5s^2$	41 Nb $4d^4 5s^1$	42 Mo $4d^5 5s^1$	43 Tc $4d^5 5s^2$	44 Ru $4d^7 5s^1$	45 Rh $4d^8 5s^1$	46 Pd $4d^{10}$	47 Ag $4d^{10} 5s^1$	48 Cd $4d^{10} 5s^2$	49 In $5s^2 5p^1$	50 Sn $5s^2 5p^2$	51 Sb $5s^2 5p^3$	52 Te $5s^2 5p^4$	53 I $5s^2 5p^5$	54 Xe $5s^2 5p^6$
6	55 Cs $6s^1$	56 Ba $6s^2$	57 La* $5d^1 6s^2$	72 Hf $4f^{14} 5d^2 6s^2$	73 Ta $5d^3 6s^2$	74 W $5d^4 6s^2$	75 Re $5d^5 6s^2$	76 Os $5d^6 6s^2$	77 Ir $5d^7 6s^2$	78 Pt $5d^9 6s^1$	79 Au $5d^{10} 6s^1$	80 Hg $5d^{10} 6s^2$	81 Tl $6s^2 6p^1$	82 Pb $6s^2 6p^2$	83 Bi $6s^2 6p^3$	84 Po $6s^2 6p^4$	85 At $6s^2 6p^5$	86 Rn $6s^2 6p^6$
7	87 Fr $7s^1$	88 Ra $7s^2$	89 Ac** $6d^1 7s^2$	104 Unq	105 Unp	106 Unh	107 Uns											

f-inner transition elements

*Lanthanides $4f^n 5d^{0-1} 6s^2$	58 Ce $4f^1 5d^1 6s^2$	59 Pr $4f^3 5d^0 6s^2$	60 Nd $4f^4 5d^0 6s^2$	61 Pm $4f^5 5d^0 6s^2$	62 Sm $4f^6 5d^0 6s^2$	63 Eu $4f^7 5d^0 6s^2$	64 Gd $4f^7 5d^1 6s^2$	65 Tb $4f^9 5d^0 6s^2$	66 Dy $4f^{10} 5d^0 6s^2$	67 Ho $4f^{11} 5d^0 6s^2$	68 Er $4f^{12} 5d^0 6s^2$	69 Tm $4f^{13} 5d^0 6s^2$	70 Yb $4f^{14} 5d^0 6s^2$	71 Lu $4f^{14} 5d^1 6s^2$
**Actinides $5f^n 6d^{0-1} 7s^2$	90 Th $5f^0 6d^2 7s^2$	91 Pa $5f^2 6d^1 7s^2$	92 U $5f^3 6d^1 7s^2$	93 Np $5f^4 6d^1 7s^2$	94 Pu $5f^6 6d^0 7s^2$	95 Am $5f^7 6d^0 7s^2$	96 Cm $5f^7 6d^1 7s^2$	97 Bk $5f^9 6d^0 7s^2$	98 Cf $5f^{10} 6d^0 7s^2$	99 Es $5f^{11} 6d^0 7s^2$	100 Fm $5f^{12} 6d^0 7s^2$	101 Md $5f^{13} 6d^0 7s^2$	102 No $5f^{14} 6d^0 7s^2$	103 Lr $5f^{14} 6d^1 7s^2$

Table Long form of the periodic table of the elements with their atomic numbers and ground state electronic configurations (according to latest 1984 IUPAC recommendation)

($4s^1$) and is completed with krypton ($4s^2 4p^6$). It has eighteen elements, i.e. ten more than in the third period. This is because of the elements in which the filling up of electrons in the 3d orbitals takes place after 4s orbital but before 4p orbitals.

$_{21}Sc$ $1s^2\ 2s^7\ 2p^6\ 3s^3\ 3d^6\ 3d^1\ 4s^2$
$_{22}Ti$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$
|
|
$_{30}Zn$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2$

Elements whose d orbitals are filled are called d-block elements. In d elements of the fourth period, the M shell is filled until if contains eighteen electrons. Similarly, the fifth period ($n=5$) has eighteen elements. It starts with rubidium ($5s^1$) and ends with xenon ($5s^2\ 5p^6$). The sixth period ($n=6$) contains thirty-two elements in which the electrons enter in 6s, 4f, 5d and 6p orbitals, in that order. It begins with two s elements (Cs and Ba) followed by lanthanum (La) in which the d orbitals of the penultimate shell begin to be filled. In the fourteen elements that follow La, 4f orbitals are filled. Then, the 5f orbitals are filled (from $_{72}Hf$ to $_{80}Hg$) and finally the period ends with six p elements ($_{81}Tl$ to $_{86}Rn$). The seventh period ($n=7$) contains two s electrons ($_{87}Fr$ and $_{88}Ra$), followed by a d element actinium ($_{89}Ac$), and fourteen f elements ($_{90}Th$ to $_{103}Lr$) and again ends with d elements ($Z=104$ to $Z=107$). This is incomplete period.

The vertical columns in the periodic table are called groups or families of elements. According to the latest IUPAC (International Union of Pure and Applied Chemistry) recommendation, the groups are numbered from 1 to 18.

Molarity of a solution. The molarity of a solution is defined as the number of moles of solute contained in one litre of the solution. The mole is molecular mass of the substance expressed in grams.

Molybdenite (Molybdenum glance) **MoS_2**. A soft lead-grey mineral with metallic lustre. The principal ore of molybdenum. Molybdenite is a semiconductor used in the manufacture of rectifiers.

Molybdenum. The term *molybdos* was used by the Greeks to represent certain substances like galena and other black minerals which left a mark on paper. Up to the middle of the eighteenth century, great confusion remained as it was not distinguished from black lead graphite. All the three minerals like molybdenite, galena and graphite left a black mark on paper.

Scheele in 1778 proved that the mineral molybdenite is different from graphite as molybdenite left a white residue (MoO_3) with nitric acid while graphite remained unaffected. He showed that molybdenite is a sulphide ore of molybdenum and occurs in nature widely. Peter Jacob in 1782 isolated the metal.

Molybdenum never occurs in native state. Its important ores are:

Molybdenite, MoS_2
Wulfenite, $PbMoO_4$
Molybdite, $FeO_3{\cdot}MoO_3{\cdot}H_2O$
Ilsemannite, $MoO_2{\cdot}5MoO_3$

Molybdenum is commonly extracted from molybedenite and wulfenite.

The following steps are involved.

Crushing The ore is first of all crushed into fine powder.

Concentration The crushed ore is concentrated by froth flotation process.

The well-powdered sulphide ore is placed along with water and pine oil in a tank and is agitated by a blast of air. The particles of the ore are perferentially wetted by oil and, therefore, rise to the surface in the form of a scum or froth while impurities are wetted by water and remain settled as the bottom. The scum or froth is separated and washed with water to get ore particles.

Roasting The crushed and concentrated ore of molybdenite is heated strongly in a current of air (roasting) when molybdenum trioxide is formed.

$$2MoS_2+7O_2 \rightarrow 2MoO_3+4SO_2$$

Purification of MoO_3

Treatment with ammonia Impure molybdenum trioxide is dissolved in ammonia and ammonium molybdate is formed.

$$2MoO_3+2NH_3+H_2O \rightarrow (NH_4)_2MoO_4$$

Purification of ammonium molybdate It is purified by crystallization or by some other suitable method.

Decomposition Ammonium molybdate is heated to decompose it to form its trioxide,

$$(NH_4)_2MoO_4 \rightarrow MoO_3+2NH_3+H_2O$$

From Wulfenite

Ullik's method The wulfenite ore is washed with dilute HCl to wash out the oxides, carbonates and phosphates of Ca, Mn, Fe, etc. and the washed material is then digested with hot conc. HCl and filtered. The filtrate is now concentrated and cooled, crystals of $PbCl_2$ which are obtained during cooling are separated and the filtrate is treated with H_2SO_4 in order to isolate remaining lead salt as $PbSO_4$. The filtrate is then treated with NH_4OH, concentrated and cooled. During cooling the crystals of ammonium molybdate separate out. On heating it yields MoO_3.

$$PbMoO_4+2HCl \rightarrow PbCl_2+H_2MoO_4$$
$$H_2MoH_4+2NH_4OH \rightarrow (NH_4)_2MoO_4+2H_2O$$
$$(NH_4)_2MoO_4 \rightarrow MoO_3+2NH_3+H_2O$$

Modified method of Wohler It involves the following steps:

(i) The concentrated ore is fused with sodium sulphide and sulphur.

$$PbMoO_4+3Na_2S+3S \rightarrow Na_2[MoS_4]+PbS+PbS+2Na_2O+SO_2$$

(ii) After cooling, the solid mass is dissolved in water whereby sulphides of sodium and calcium along with sodium thiomolybdate go into solution.

(ii) The filtrate is acidified with H_2SO_4 so that molybdenum trisulphide is precipitated.

$$Na_2[MoS_4]+H_2SO_4 \rightarrow MoS_3+Na_2SO_4+H_2S$$

(iv) The precipitate is filtered, washed with waier, dried and heated in absence of air. It is then roasted in air to molybdic oxide.

$$MoS_3 \rightarrow MoS_2+S$$
$$MoS_2+7O_2 \rightarrow 2MoO_3+4SO_2$$

Molybnenum metal may be prepared in several ways.

(i) By reducing the oxide, MoO_3 in an atmosphere of hydrogen.

$$MoO_3+3H_2 \xrightarrow{775\text{-}1475\ K} Mo+3H_2O$$

Molybdenum is obtained as a fine dark powder.

Uses as alloying component of steels, in electrical and radio devices. Molybdenum is a microelement.

Monazite. It is a mineral containing rare earth metal phosphates, mainly phosphates of cerium family metals, (Ce, La) PO_4. Together with rare earths (more than 50%) contains ThO_2 (5 to 10%), sometimes U_3O_8 (up to 1%). Colour reddish-brown, resinous lustre, brittle. Used as a source of rare earth metals and thorium.

Monel. Trademark for a nickel-copper alloy containing up to 30% copper. It has high mechanical properties and resistance to corrosion, ductite. Used in ths chemical, petroleum, ship-building industries, in the manufacture of medical and other instruments.

N

Neodymium [Greek *neos*, new+*didimos*, a twin] Nd. A Group III element of 6th period of the Periodic Table of Elements, atomic number 60, atomic mass 144.24, belongs to lanthanides. Discovered in 1885 by Welsbach.

Properties A silvery metal. An analogue of other lanthanides, the oxidation state in compounds +3; salts have pink colouration.

Uses As an alloying component, in electronics, in the manufacture of coloured glass, porcelain, etc.

Neon [Greek *neoς*, new] Ne. A Zero Group element of the 2nd period of the Periodic Table of Elements, atomic number 10, atomic mass 20.179, an inert (noble) gas. Discovered in 1898 by Ramsay and Travers. A monoatomic gas, does not participate in usual reactions. The hydrate, $Ne.6H_2O$, and some other compounds with bonds of molecular nature were isolated.

Uses In filling incandescent lamps, luminescent electric tubes (gives red luminescence and therefore used in advertizing, in traffic signs), employed in electronics and vacuum devices.

Neptunium (At. No. 93). This is the first transuranic element and was discovered by McMillan and Abelson is 1940. They bombarded a layer of uranium oxide with slow neutrons and got a rodioisotope of neptunium with half-life of 2.3 days.

This isotope was recognized as a beta-decay product of radioisotope of uranium with a half-life of 23 minutes. The two nuclear reatctions are:

$$ {}^{238}_{92}U + {}^{1}_{0}n \longrightarrow {}^{239}_{93}U \quad \text{(half-life of 23 minutes)} $$

$$ {}^{238}_{92}U \longrightarrow {}^{239}_{93}Np + e^- \quad \text{(half-life of 2.3 days)} $$

Another more stable isotope of ${}^{237}_{93}Np$ was discovered by Seaborg and A.C. Wahl in 1942. It was obtained by the action of high speed neutrons in an (n, 2n)-type reaction as given below:

$$ {}^{238}_{92}U + {}^{1}_{0}n \longrightarrow {}^{237}_{93}U + {}^{1}_{0}2n \quad \text{(half-life of 7 days)} $$

$$ {}^{237}_{93}U \longrightarrow {}^{237}_{93}Np + e^- $$

(half-life of 2.25×10^6 years)

Nickel. Nickel was discovered by Cronstedt in 1751. It was isolated from an ore which was called kupfernickl, German term meaning false copper, and was called nickel.

Nickel is present in meteoric iron. Chief ores of nickel are:

Smaltite, (Fe, Co, Ni) As
Kupfernickel or nicollite, NiAs
Pentlandite, (Ni, Cu, Fe) S
Garnierite, (NiMg) H_2SiO_4.

In these, the metal is associated with copper, iron, cobalt and small amounts of silver, gold and the platinum metals. The ores are usually very lean and as obtained from the mine codtain only about 2 per cent of nickel and about double this amount of copper. It comes principally from Sudbury district of Ontario, Canada, and in smaller amounts from New Caledonia, Norway and Germany.

Principal uses of nickel are: (i) for nickel plating (ii) as a metal resistant to alkaline corrosion, e.g. in making nickel crucibles, tongs and spatulas for laboratory use, (iii) in the manufacture of important alloys and (iv) as a hydrogenation cataylst. It is also used in the electrical industry as the anode of Edison batteries and in radio valves. Some important alloys of nickel are:

Invar steel It contains 35 per eent Ni and 3.0 per cent cabon and has a negligible coefficient of expansion. It is used in surveying instruments, pendulums, chronometer components, etc.

Monel metal (70 per cent Ni, 30 per cent Cu). It is resistant to corrosion and is used in chemcial plants.

Constantan (40 per cent Ni, 60 per cent Cu). It is used in electrical resistances.

Nichrome (80 per cent Ni, 20 per cent Cr). It is very resistant to oxidation, and is, therefore, used in making heating elements in electric heaters.

Nickel silver or *German silver* (10-30 per cent Ni with Cu and Zn). It is used for making cheap ornaments, domestic utensils and tableware.

Cainage alloy (Cu 75 per cent; Ni 25 per cent). It is used for making coins.

Nickel carbonyl, $Ni(CO)_4$. It is formed when a stream of carbon monoxide is passed over finely divided nickel at 325 K.

$$Ni + 4CO \xrightarrow{325\ K} Ni(CO)_4$$

It is a colourless volatile liquid (b.p. 316 K), very poisonous in nature.

It decomposes when heated to about 355-375 K, depositing the metal.

$$Ni(CO)_4 \xrightarrow{355\ K} Ni + 4CO$$

It reacts with chlorine to form $NiCl_2$.

$$Ni(CO)_4 + Cl_2 \longrightarrow NiCl_2 + 4CO$$

Dry hydriodic acid reacts with it to give NiI_2.

$$Ni(CO)_4 + 2HI \longrightarrow NiI_2 + H_2 + 4CO$$

It is used in the extraction and purification of nickel by Mond's Process.

Nickel plating. A process for the production of nickel coatings on metal objects to prevent corrosion and improve the finish.

Nickel silver. Nickel alloys containing copper, zinc, etc. Resistant to corrosion. Used for coinage.

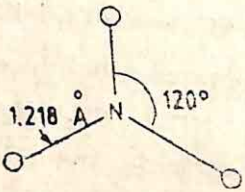
Niobium [Latin *Niobe*, daughter of Tantalus: from association with tantalum] **Nb** A 4 d element of the 5th period of the Periodic Table of Elements, atomic number 41, atomic number 41, atomic mass 92.946. One stable isotope, ^{93}Nb. Discovered in 1801 by Hatchett.

Properties A grey-white high-melting metal stable in the air. Resembles tantalum in its chemical properties, the most stable oxidation state +5. Insoluble in acids except for hydrofluoric acid. The oxide, Nb_2O_5, shows acidic properties.

Occurrence Always accompanies tantalum.

Uses The principal component of many heat and corrosion resistant alloys. Niobium and its alloys are mainly used in nuclear energy devices, electronics, in the manufacture of apparatus for the chemical industry, jet engines, in the rocket engineering, in vacuum systems.

Nitrates. Nitrates of practically all metallic elements are known and are all water-soluble and are frequently hydrated. Some nitrates can be obtained anhydrous and some of them sublime [e.g. $Cu(NO_3)_2$] without decomposition. Alkali nitates on decomposition give nitrites while NH_4NO_3 gives N_2O and H_2O, Al and Zn in alkaline solution reduce them to NH_3. The nitrate ion is planar and symmetrical.



Nitrates give brown fumes with concentrated sulphuric acld.

Nitrates reduce to nitrites with nascent hydrogen (zinc and hydrochloric acid) and give the tests of nitrites.

To a nitrate solution is added freshly prepared solution of ferrous sulphate and concentrated sulphuric acid is poured along the side of the test tube. A dark brown ring of $[Fe(H_2O)_5NO]SO_4$ is formed at the junction of two liquids.

Nitrogen [Greek *nitron*, native soda, natron] N. A Group VA element of the 2nd period of the Periodic Table of Elements, atomic number 7, atomic mass 14.0067. two stable isotopes, ^{14}N (99.635 per cent) and ^{15}N. Dicovered by D. Rutherford in 1772.

Properties A colourless gas, odourless, slightly soluble in water, lighter than air, m.p. 63 K. b.p. 77.2 K. Nitrogen molecules are diatomic with a strong triple bond between the atoms. N≡N: The oxidation states in compounds range from —3 to 5. Almost unreactive at room temperature. At elevated temperatures combines with active metals to give nitrides, e.g. Ca_3N_2. Under certain conditions reacts with hydrogen.

$$N_2+3H_2\rightarrow 2NH_3$$

(catalyst, pressure, temperature)

and oxygen

$$N_2+O_2\rightarrow 2NO$$

(electric discharge)

Forms several oxides.

Occurrence The atmosphere contains 78 volume per cent N_2, occurs as nitre, found in proteins, nucleic acids, chlorophyll, enzymes, hormones, and many vitamins.

Manufacture By fractional distillation of liquid air.

Uses Mainly in the synthesis of ammonia. Liquid nitrogen is used as a source of cold, free nitrogen as an inert atmosphere for certain chemical processes, for filling incandescent lamps, for electric welding of metals. Air nitrogen in the chief nitrogen source for the manufacture of nitrogen fertilizers.

Nitrogen cycle. The nitrogen cycle is a complex series of reactions which, if allowed to occur without interference; tend to keep a balance between the nitrogen in the atmosphere, in the soil, and in living organisms.

Nitrogen fertilizers. Inorganic and organic compounds containing nitrogen put in the soil to make it fertile. Mineral nitrogen fertilizers include amide, ammonia, and nitrate fertilizers. Prepared mostly from synthetic ammonia.

Nitroposphate. A complex fertilizer containing nitrogen, phosphorus and usually potassium. Generally obtained by the action of nitric acid or a mixture of nitric and sulphuric or phosphoric acids on phosphate rock followed by the neutralization with ammonia and addition of potassium salts.

Nitrous acid, HNO_2. A weak monobasic acid, exists only in dilute aqueous solutions which decompose when heated with the evolution of NO and NO_2. Can oxidize certain species, e.g. I^-, and undergo oxidation to HNO_3 under the action of strong oxidizing agents such as H_2O_2 and $KMnO_4$. Metal salts of nitrous acid, nitrites are used in the organic synthesis.

Nobelium (after A. Nobel) **No.** A transuranic element of the actinde series, atomic number 102. The isotopes with the mass numbers of 251 to 259 were synthesizcd; the longest lived isotope, ^{259}No, decays with a half-life of about 1.5 h. The oxidation states are $+ 2$ and $+3$.

Noble gases. In the noble gases, He, Ne, Ar, Kr, Xe and Rn, all sets of s, p, d and f orbitals which occur are filled to capacity. Except for the helium in which the configuration is $1s^2$, the other shell in all other cases has a configuration of ns^2 np^6. These elements occupy the last column in the Periodic Table making the closing of the p sub-shell.

Non-aqueous solvents. Water has long been recognized as the "universal solvent." This recognition is due largely to the plentiful occurrence of water in nature and its unusual solvating characteristics. No other solvent is quite so versatile in terms of availabitity, wide liquid range, ease of handling, and ability to dissolve substances. No other solvent displays so wide a range in physical and chemical properties. For these many reasons water occupies an exceptional position among solvating media. However, we hasten to add that water is not unique in its properties. Many other substauces have similar solvent properties, but it must be admitted that such properties are not usually so pronounced as in water. The difference between water and certain other solvents is more often a matter of degree rather than a difference in behaviour. Unfortunately very few liquids have been investigated as to their behaviour as solvents for inorganic substances. It is doubtful that any other branch of inorganic chemistry offers wider opportunities for investigation than does the study of inorganic substances in nonaqueous media.

Many liquids have the ability to dissolve inorganic materials, but we are more interested in those solutions in which ionic reactions take place. Solvents in which ionization takes place may be described as possessing "waterlike" properties, and it is upon the basis of such properties that solvents are sometimes classified.

It is believed that all ionizing media exist as ions, to some extent, when in the pure state: consequently such solvents are invariably weak conductors of electricity. Familiar examples of solvents of this type are water, liquid ammonia, hydrogen fluoride, liquid hydrogen cyanide, and liquid sulphur dioxide.

Non-metal (formerly called metalloid). A simple substance lacking the properties characteristic of melals (glitter, malleabiliity. electric and thermal conductivity). Many non-metals are gases under usual conditions. Non-metals also differ from metals in their chemical properties: their higher oxides are usually acidic while the lower oxides of metals are basic.

Normality. A form of expressing solution concentrations by the number of equivalents of a solute per litre of a solution, very common in the analytical chemistry.

Normality equations. According to the law of equivalents, substances react in the ratio of their equivalent weights. This means that if the solution of a substance *A* is titrated against the solution of a substance *B*, then at the end point we can write as follows:

No. of gram-equivalents of solution *B*

=No. of gram-equivalents of solution *B*

or

$$N_1V_1=N_2V_2$$

Where N_1 is the normality of solution *A*, V_1 is the volume of solution *A*, N_2 is the normality of solution *B* and V_2 is the volume of solution *B*.

This equation is called Normality equation. It is used for calculating the normality of unknown solution. If N_1, V_1 and V_2 are known, the normality N_2 of a solution can be calculated as:

$$N_2=\frac{N_1V_1}{V_2}$$

Normality of a solution. The normality of a solution is defined as the number of gram-equivalents of the solute per litre of the solution.

Nuclear binding energy. Just as bond energy is the energy required to break a bond, nuclear binding energy is the energy necessary to break up a nucleus into its constiuent protons and neutrons. The binding energy of the nucleus is the energy released when the nucleus is formed from isolated protons and neutrons. It is equivalent ($E=mc^2$) to the loss in mass when the nucleus is so constructed.

Nuclear fission. It is the nuclear reaction which involves splitting of heavier and bigger nucleus into smaller and lighter nuclei by bombardment of slow-moving neutrons. One of the possible reactions which takes place during nuclear fission of heavier U-235 is given below.

$$^{235}_{92}\text{U}+{}^{1}_{0}\text{n}\longrightarrow {}^{139}_{56}\text{Ba}+{}^{94}_{27}\text{Kr}+3\,{}^{1}_{0}\text{n}$$

Nuclear fuel. Energy in the form of heat is contained during nuclear reactions involving fission. Uncontrolled nuclear fission leads to the formation of atomic bombs. Controlled nuclear fission reactions can be used for peaceful uses, for generation of electricity. These plants are known as atomic power plants. The fuel used in these nuclear power plants ars generally $^{235}_{92}\text{U}$ and $^{239}_{94}\text{Pu}$. Both these isotopes undergo fission by slow moving neutrons. During this poress of fission, a part of the weight of the nucleus is destroyed and converted into energy (mostly-heat energy) according to the Einstein equation.

$$E=mc^2$$

Nuclear fusion. Fusion reaction is quite opposite of nuclear fission. In such a reaction light nuclei combine to form heavier nucleir accompanied by the release of enormous energy.

For example, two light deuterium nuclei $\left(^{2}_{1}\text{H}\right)$ fuse together to a helium nucleus $\left(^{4}_{2}\text{He}\right)$ releasing $93{\cdot}10\times01^{8}$ kJ energy per mole helium nucleus formed.

$$^{2}_{1}\text{H}+^{2}_{1}\text{H}\longrightarrow\,^{4}_{2}\text{He}+23{\cdot}01\times10^{8}\ \text{kJ mol}^{-1}$$

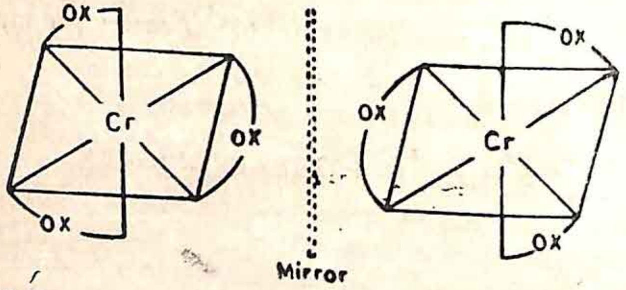
O

Open-hearth process, Siemens-Martin process. It is a process for steel manufacture suggested by the French metallurgist Martin in 1864. Unlike the Bessemer process, carried out in a furnace with some smelting by hot producer gases. The open-hearth process has the advantage of providing the possibility to remove undesired admixtures, take assays, and add needed components to produce special kinds of steel during smelting.

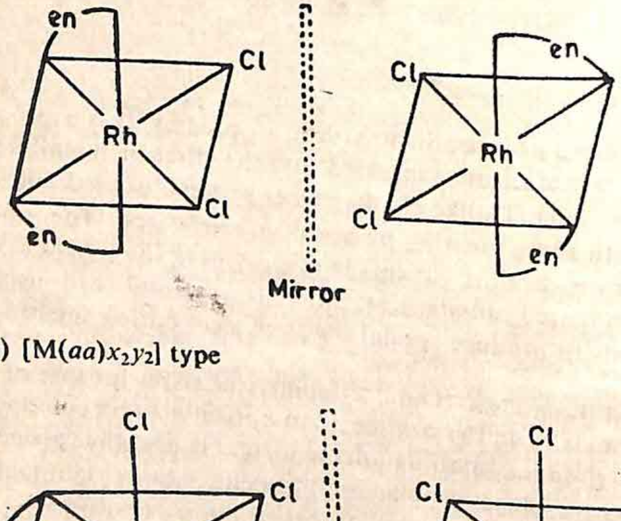
Optical isomerism. Optical isomerism arises because of the lack of symmetry in the complex. An optically active compound is not superimposable on its mirror image. It has the property of rotating the plane of polarized light either to its right (called dextro or *d*-isomer), or to its left (called laevo or *l*-isomer).

This type of isomerism is common in octahedral complexes of the type $[M(aa)_3]$, $[M(aa)_2x_2]$ and $[M(aa)x_2y_2]$ (where $aa=$ symmetrical bidentate ligand, x or $y=$monodentate ligand).

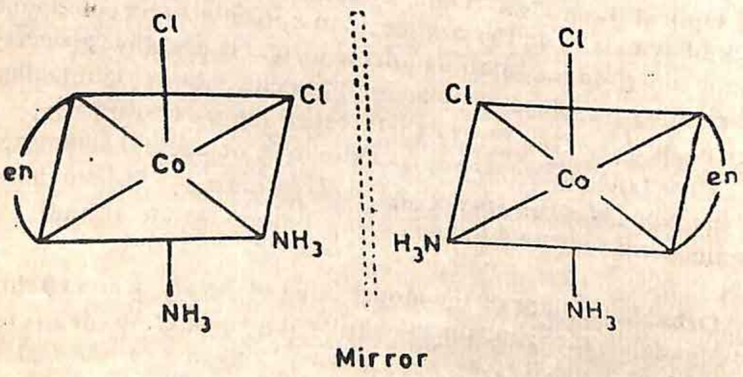
Orbital. In place of the model using planetary orbits (Bohr-Sommerfeld), the probability-density representation describes the motion of electron as being concentrated in a certain region with a certain shape around the nucleus. The region in space (*a*) $[\mathrm{M}(aa)_3]$ type



(*b*) $[\mathrm{M}(aa)_2x_2]$ type



(*c*) $[\mathrm{M}(aa)x_2y_2]$ type



around the nucleus of the atom in which there is maximum probability of finding the electron is called an orbital. An orbital can be represented by a mathematical function, as well as pictorially by the probability density representations.

Ore dressing. The ores are generally contaminated with rocky and earthy impurities which are called matrix or gangue. The process of removing these impurities from ore is called ore dressing. The methods employed for ore dressing are:

Froth flotation process,

Electromagnetic separation,

Gravity separation,

Leaching process,

Liquation process.

Orthophosphoric acid, H_3PO_4. It is also known as phosphoric acid and can be prepared as:

By dissolving phosphorus pentoxide in hot water.

$$P_4O_{10}+6H_2O \longrightarrow 4H_3PO_4$$

By the hydrolysis of phosphorus pentachloride with water.

$$PCl_5+4H_2O \dashrightarrow H_3PO_4+5HCl$$

In laboratory, it is prepared by the reaction of white phosphorus and concentrated nitric acid (sp. gr. 1.2).

$$P_4+20HNO_3 \dashrightarrow 4H_3PO_4+20NO_2+4H_2O$$

Osmium [Greek *osme*, odour; so called because of irritating smell of OsO_4] **Os.** A 5 d element of the 6th period of the Periodic Table, atomic number 76, atomic mass 190.2. Discovered in 1804 by Tennant. A platinum family metal.

Properties Tin-white metal with a bluish cast, the heaviest of all the metals known, hard, brittle. Gives OsO_4 when heated in the air. The most stable oxidation states are +4, +6, and +8. Like other platinum metals readily forms complex compounds.

Occurrence As iridosmine (a natural alloy with iridium).

Uses Because of the high hardness and corrosion resistance the metal and its alloys with other platinum metals and also with Co and W are used in the manufacture of precision measurement instruments, Osmium and its compounds, e.g. OsO_4, are good catalysts.

Oxidation state. It is defined as the apparent charge on the central atom when all other atoms of the compound have been removed as ions, e g. N^{3-}, O^{2-}, Cl^- and H^+. Thus oxidation number can be found equally well for ionic or covalent compounds, and without knowing the type of bonds. Thus the oxidation state of Mn in $KMnO_4$ may be calculated as follows: —Remove K^+ (leaving one negative charge behind) and remove four O^{2-} ions (leaving eight positive charges behind) so that the charge left on Mn is $-1+8=7$. Thus oxidation state of Mn in $KMnO_4$ is $+7$. In Mn_2O_7, again it is $+7$. Similarly oxidation state of Cr is $+6$ in CrO_3 and $K_2Cr_2O_7$ while that of Os is $+8$ in OsO_4.

Oxide. The term "oxide" usually refers to a compound composed of oxygen and one other element, in which the oxygen is in the -2 oxidation state.

Oxide coating. A coating of a metal surface with a protective oxide film to prevent corrosion or for decorative purposes.

Oxygen [Greek *oxys*, sharp, acid] **O**. A Group VIA element of the 2nd period of the Periodic Table of Elements, atomic number 8, atomic mass 15.9994. Occurs in nature as a mixture of three isotopes, ^{16}O (99.759%), ^{17}O (0.037%), and ^{18}O (0.204%). Discovered by Scheele in 1771 and independently, by Priestley in 1774.

Properties A diatomic gas, O_2, colourless and odourless, b.p. 90 K, m.p. 54.3 K, gives ozone, O_3, under the action of electric discharge. Slightly soluble in water. Effectively absorbed by charcoal and molten noble metals. Forms compounds with all the chemical elements except for light noble gases; reacts directly with most elements. The oxidation state in compounds —2. Readily oxidizes organic substances.

Occurrence The most abundant element, forms 23 per cent of the atmosphere by weight, contained in bound state in water, sand, alumina, rocks, ores, etc.

Manufacture From air by liquefaction.

Uses Various applications in the chemical industry, welding and cutting of metals, in medicine, in aviation, submarines. Liquid oxygen is used as an oxldant in rocket fuels. Oxygen is essential to all living organisms.

Oxyliquit. An explosive made by impregnating a porous solid fuel with liquid oxygen, used in mining.

Ozone [Greek *ozein*, to smell] O_3. A simple substance, an allotropic form of oxygen.

Properties A gas with a characteristic odour, unstable; a strong oxidizing agent, reacts with most metals to give the corresponding oxides, destroys rubber.

Occurrence Formed in the atmosphere under the action of thunderstorm electricity, ultraviolet irradiation.

Mauufacture By subjecting air or oxygen to a silent electric discharge in special apparatus (ozonizers).

Uses As an oxidizing agent for air purification and conditioning, decontamination of drinking water, in the manufacture of some organic substances (camphor, vanilline, fatty acids, etc.).

Oxyacid. Compounds which contain the hydroxyl (OH) group covalently bonded to another atom and in which the O—H bond is broken in aqueous solution are called oxyacids.

Oxyacids of chlorine. The following oxyacids of chlorine are known.

Name	*Formula*	*Oxidation State of chlorine*
Hypochlorous acid	$HClO$	+1
Chlorous acid	$HClO_2$	+3
Chloric acid	$HClO_3$	+5
Perchloric acid	$HClO_4$	+7

Hypochlorous acid, $HClO$ is a weak acid which is produced in low concentrations when free halogen reacts with water. The reaction equilibrium can be shifted in favour of $HClO$ by adding Ag_2O or HgO to the reaction mixture.

Sodium hypochlorite, used commercially in cotton bleaching is prepared by electrolysing cold sodium chloride solutions. In this case the products are vigorously mixed so that the chlorine produced at the anode reacts with hydroxide ion produced at the cathode. Chlorous acid, $HClO_2$ is stronger than the hypochlorous acid. It cannot be isoloted but its salts can be produced by passing ClO_2 gas into a solution of an alkali.

$$2ClO_2+2OH^- \longrightarrow ClO_2^- + ClO_3^- + H_2O$$

If ClO_2 is passed through alkaline solution of sodium peroxide, ClO_3^- is not produced. Chlorites are dangerous as they detonate on heating and explode in contact with combustible material. Solutions of chloric acid can be prepared by adding H_2SO_4 to a solution of barium salt.

$$Ba(ClO_3)_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HClO_3$$

Chlorates are commercially prepared by the electrolysis of hot concentrated solution of a chloride.

Chlorates are useful compounds. When SO_2 is passed through the aqueous solution of a chlorate, ClO_2 is produced. On heating to moderate temperatures and in the absence of a catalyst, chlorates decompose to give perchlorates.

$$4KClO_3 \longrightarrow 3KClO_4 + KCl$$

Another method of preparing a perchlorate is by electrolysis of a cold solution of a chlorate. The free acid is obtained by the action of H_2SO_4 on a perchlorate.

Oxysalts. Oxysalts are salts of oxyacids. They are composed of cations and oxyanions. (Example: $NaNO_3$ is composed of Na^+ and NO_3^- ions).

P

Palladium. Palladium is the last noble of the platinum metals resembling platinum in its mechanical properties,

Palladium was discovered by Woolastonin 1803 in the crude platinum metal. The name palladium was given to the element in honour of the recently-discovered asteroid "Pallas".

It is a rare metal. It is found to occur in the free state in the form of octahedral cubic crystals in Brazil and Ural mountains. Selenopalladium is another native source of the element. In the combined states, it occurrs as:

Braggite (Pt, Pd, Ni) S

Stibiopalladinite, $Pd_3 Sb_2$

Potarite, PdHg

Parpazite, which is palladium-gold ore.

Traces of palladium are found in various platinum ores. In addition to these, it is also present in the earth's crust.

Extraction

From Platinum Ores The palladiferrous material is treated with aqua regia. The insoluble residue is separated by filtration. The acid filtrate is treated with an excess of NH_4Cl and ethanol. Platinum and iridium are precipitated as ammonium chloro-compounds by adding NH_4Cl. The palladous salt remains in solution. The precipitate is separated and from the filtrate platinum and iridium are completely removed by adding NH_4Cl and alcohol. The filtrate is treated with mercuric cyanide to precipitate the palladium as cyanide. Pure Pd is obtained by igniting the cyanide.

Woolaston's process Native platinum is treated with aqua regia and precipitated as $(NH_4)_2PtCl_6$ by adding NH_4Cl. The filtrate is reduced with zinc or iron. This is treated with dil. HNO_3 and filtered. Copper, Iron, lead and zinc go into solution while palladium and platinum remain insoluble. These are treated with conc. HCl and KNO_3, Palladium and platinum go into solution. K_2PdCl_4 is crystallized out by evaporation of the solution. The crystals of potassium palladium chloride are treated withKOH. Palladium oxide is obtained which on ignition in stream of hydrogen yields palladium melal.

Palladium metal is obtained by ignition of:

(i) Palladium cyanide, $Pd(CN)_2$

$$Pd(CN)_2 \xrightarrow{\text{ignite}} Pd + (CN)_2$$

(ii) Palladium iodide:

$$PdI_2 \xrightarrow{\text{ignite}} Pd + I_2$$

(iii) Ammonium salt, $(NH_4)_2PdCl_4$

$$(NH_4)_2PdCl_4 \rightarrow Pd + 2NH_3 + 4HCl$$

Metallic Palladium It is prepared by igniting $[Pd(NH_3)_2]Cl_2$.

$$[Pd(NH_3)_2]Cl_2 \rightarrow Pd + 2NH_3 + Cl_2$$

It can also be obtained by heating ammonium chloropalladinate in current of hydrogen.

Spongy palladium It is obtained by the ignition of ammonium chloropalladinate $(NH_4)PdCl_4$. It can also be prepared by the reduction of palladium chloride with sodium formate in hot condition.

Palladised asbestos It is obtained by soaking asbestos with hydrochloro-palladous acid, H_2PdCl_6 followed by ignition.

Colloidal palladium It is prepared by sparking palladium electrodes under ice-cold water, containing traces of alkali. It can also be obtained by the reduction of palladous chloride with $TiCl_2$ or $NH_2NH_2.HCl$.

Polladium black It is obtained by precipitation from a palladium salt solution with a weak reducing agent such as sodium formate.

Palladium stands between silver and platinum in appearance. Its density is 12.03.

It soffens before melting (m.p. 1828 K).

Among the platinum metals it is most fusible.

It is malleable, ductile and can be welded at red heat.

Palladium has an adsorptive capacity for many gases especially for hydrogen. When finely divided, it adsorbs 700 or more times its own volume of hydrogen. A part of adsorbed hydrogen is probably held in solid solution in the metal. The adsorbed hydrogen is very active and hence palladium has a pronounced catalytic activity.

Palladium with adsorbed hydrogen is very efficient reducing agent. Colloidal palladium adsorbs 3 to 8 times as much hydrogen as ordinary palladium.

Palladium is an element of the nickel group, electronic configuration $4d^{10}$. The chemistry of palladium is similar to that of platinum although $+6$ and $+5$ oxidation states are missing. There are extensive ranges of complexes.

Palladium is chemically inert.

It is not attacked by mineral acids except HNO_3 which does slowly dissolve it. In the finelly divided state, palladium is slowly attacked by HCl in presence of oxygen.

When heated to red heat in air, it is oxidized to palladium monoxide. Molten metal dissolves oxygen which is given off on solidification as in the case of silver.

At red heat fluorine and chlorine attack the metal and form difluoride and dichloride.

It shows valences of 2, 3, 4 but bivalent compounds are very stable.

Palladium is rapidly attacked by fused alkali oxides and especially peroxides.

Palladium stands next to platinum in applications.

Colloidal palladium is used as a catalyst in the hydrogenation of nitro-groups, aldehydes, ketones and many organic compounds. It also finds application in the cracking of petroleum.

It is also used in electroplating.

It is used in dental, jewellery and electrical industries as a substitute for platinum.

Palladium compounds are used as toning agent in photography.

Palladium nitrate is used in the identification and estimation of carbon monoxide in mines and garages.

The oxides of palladium namely Pd_2O, PdO and PdO_2 are known.

Palladium(II) oxide The only well-known oxide is PdO which is formed by direct combination of the elements at about 775 K or by ignition of salts. A hydrated form is precipitated from solution.

It is black powder insoluble in all acids and even in aqua regia. It acts as a strong oxidizing agent as it decomposes on heating into the metal and oxygen.

Palladium(II) hydrous oxide, $Pd.nH_2O$. It is a yellow gelatinous precipitate which is obtained by adding dilute hydroxide to a solution of palladous nitrate. Unlike the oxide, it dissolves readily in acids when freshly precipitated.

The yellow gelatinous precipitate dries in air to a brown coloured. On heating at 375 K, it loses more water and becomes black. It cannot, however, be completely dehydrated without loss of water.

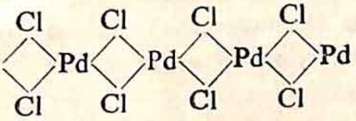
Palladium suboxide (Pd_2O). It is prepared by heating palladium at 725 K in oxygen. It can also be obtained by heating palladium monoxide to redness. Pd_2O decomposes with acid into monoxide and metal.

Palladium dioxide (PdO_2). It is obtained by treating a solution of potassium palladate with a slight excess of KOH. The brown precipitate so obtained is washed with water and then dried over conc. H_2SO_4.

Three chlorides namely PdCl, $PdCl_2$ and $PdCl_3$ are known.

The monochloride, (PdCl) is obtained by heating $PdCl_2$ at red heat. It is reddish brown crystalline solid.

Palladous chloride ($PdCl_2$). It is made by the action of Cl_2 on the metal heated to red heat. It is hygroscopic and soluble in water. From the aqueous solution, crystals of $PdCl_2.2H_2O$ are obtained. In the anhydrous conditions, the structure of the compound may be given as below:



$PdCl_2$ is soluble in HCl acid or alkali metal chloride solution due to the formation $[PdCl_4]^{2-}$.

Palladium trichloride ($PdCl_3$) is unstable and is formed when palladium monoxide is treated with HCl.

Palladium difluoride (PdF_2). is obtained by adding HF to a concentrated solution of $Pd(NO_3)_2$. It is a brown powder and is slightly soluble in water.

Palladium trifluoride (PdF_3) is produced by the action of fluorine on $PdCl_2$ at 475-525 K,

Palladium(II) sulphate or *Palladous sulphate*, $PdSO_4$

It is prepared by dissolving palladium hydroxide in dilute sulphuric acid. It is a brown solid which is deliquescent.

Palladium(II) cyanide or *Palladous cyanide*, $Pd(CN)_2$

It is prepared by adding potassium cyanide to a solution of palladous chloride. The precipitate dissolves in excess of potassium cyanide due to the formation of the complex compound, $K_2Pd(CN)_4.3H_2O$.

$$PdCl_2+2KCN \rightarrow Pd(CN)_2+2KCl$$
$$2KCN+Pd(CN)_2 \rightarrow K_2Pd(CN)_4$$

Paramagnetism. Paramagnetism is a weak attraction into a magnetic field ("toward a magnet"). Any substance which contains unpaired electrons is paramagnetic. In general the total magnetic moment associated with an unpaired electron is the sum of the magnetic moment related to the electron's spin angular momentum and the magnetic moment related to its orbital angular momentum. In many cases however, the orbital moment "ignores" an externally applied magnetic field, because the fields of surrounding atoms are strong enough to prevent significant interation between the orbital moment and the external field. In these cases the orbital moment is said to be quenched, and the measured magnetic moment is effectively a "spin-only" moment. Paired electrons do not contribute to paramagnetism, because the two magnetic moments just cancel each other. Both paired and unpaired electrons do contribute to diamagnetism, however.

Passivity. The apparent reactivity of certain metals, including iron, can be greatly reduced by treating them with a powerful oxidizing agent, such as concentrated nitric acid. The metal is then said to have become passive. Passivity is apparently caused by the formation of a tough, impervious surface coating of oxide, which protects the metal against further oxidation.

p-Block. The elements of Groups IIIA, IVA, VA, VIA, VIIIA and zero (noble gases) constitute the p-block of the periodic table. In these elements the differentiating electron enters a p orbital of the outermost shell. The characteristic electronic configuration of the outermost shell of these elements varies from $n\mathrm{s}^2\ n\mathrm{p}^1$ to $n\mathrm{s}^2\ n\mathrm{p}^6$ (i.e. from Group IIIA to zero group).

Pauli exclusion priniple. Pauli exclusion principle states that no two electrons in the same atom may have identical sets of all four quantum numbers. That is to say even if two electrons have the same values of n, l and m they will differ in their m_s values. This situation indicates that the two electrons in a single orbital are paired. Two electrons in a 1s orbital, for example, have (n, l, m, m_s) quantum sets of (1, 0, 0, $+\frac{1}{2}$) and (1, 0, 0, $-\frac{1}{2}$). According to the exclusion principle, therefore, an orbital may hold no more than two electrons.

The maximum number of electrons that a shell can hold is $2n^2$. Each of orbital can hold two electrons. The maximum number of electrons in a shell is thus, equal to twice the number of orbitals (n^2) in the shell. The maximum number of electrons in a subshell can be calculated by multiplying the number of orbitals in the subshell by 2. That is how the Pauli exclusion principle puts a limit on the maximum number of electrons that can be accomodated in a given shell or subshell.

Pearson's principle. Pearson has suggested a simple rule of thumb to predict qualitatively the relative stability of acid-base reactions. Accordingly, "Hard acids prefer to bind to hard bases and soft acids prefer to bind to soft bases." Thus, the complex *AB* is the most stable when both *A* and *B* are either hard or soft. However, when one of the reactants is very hard and the other very soft, the complex will not be much stable.

Perchloric acid, HClO₄. It is obtained by the distillation or evaporation of chloric acid.

$$3HClO_3 \longrightarrow HClO_4 + Cl_2 + 2O_2 + H_2O$$

It ean also be prepared by the reaction of potassium perchlorate with concentrated sulphuric acid.

$$KClO_4 + H_2SO_4 \longrightarrow KHSO_4 + HClO_4$$

Anhydrous perchloric acid is a colourless hygroscopic liquid (b.p. 292 K). It is unstable and decomposes on keeping for a few days even in dark. On heating it decomposes with explosion hence it is distilled under reduced pressure (15-20) at 287-291 K. Its aqueous solution is quite stable and does not decompose. It is the strongest simple acid known. It is a powerful oxidizing agent. It produces blisters on the skin. It gives chlorine heptoxide with phosphorus pentoxide.

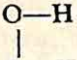
$$4HClO_4 + P_4O_{10} \longrightarrow 4HPO_3 + 2Cl_2O_7$$

Periodic acids. Three periodic acids are known. Out of these paraperiodic acid, H_5IO_6 or $HIO_4.2HO_2$ is most common while other periodic acide are dehydration products of this acid.

$$2H_5IO_6 \xrightarrow[-3H_2O]{353\text{ K}} H_4I_2O_9 \xrightarrow[-H_2O]{373\text{ K}} 2HIO_4 \xrightarrow{413\text{ K}} 2HIO_3 + O_2$$

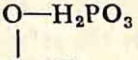
Paraperiodic acid	Dimesoperiodic acid	Metaperiodic acid	Iodic acid

Peroxophosphoric acids. These acids are derived from hydrogen peroxide by the replacement of one and two hydrogen atoms by H_2PO_3 group. Thus



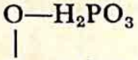
$$\begin{array}{l} \text{O—H} \\ | \\ \text{O—H} \end{array}$$

(H_2O_2)



$$\begin{array}{l} \text{O—}H_2PO_3 \\ | \\ \text{O—H} \end{array}$$

(H_3PO_5)



$$\begin{array}{l} \text{O—}H_2PO_3 \\ | \\ \text{O—}H_2PO_3 \end{array}$$

($H_4P_2O_8$)

Phosphorus forms two peroxophosphoric acids, i.e. peroxomonophosphoric acid, H_3PO_5 and peroxodiphosphric acid $H_4P_2O_8$.

Peroxomonophosphoric acid is obtained by the action of phosphorus pentoxide and 30 per cent hydrogen peroxide at low temperature. Peroxodiphosphoric acid is obtained by the action of hydrogen peroxide and phosphorus pentoxide.

Both acids are strong oxidizing agents.

Permanent hardness. Water is said to show permanent hardness if it does not contain HCO_3^- ions in addition to the Ca^{2+}, Mg^{2+}. or Fe^{2+} ions. Such hardness is also known as *noncarbonate hardness*.

Permonosulphuric acid, H_2SO_5. It is obtained by the reaction of sulphuric acid on potassium perdisulphate or on 5 per cent hydrogen peroxide.

$$H_2SO_4+K_2S_2O_8 \longrightarrow K_2SO_4+H_2S_2O_8$$
$$H_2S_2O_8+H_2O \longrightarrow H_2SO_4+H_2SO_5$$
$$H_2SO_4+H_2O_2 \longrightarrow H_2SO_5+H_2O$$

It is a white crystaliine hygroscopic mass (m.p. 318 K).

It reacts with hydrogen peroxide to evolve oxygen.

$$H_2SO_5+H_2O_2 \longrightarrow H_2SO_4+H_2O+O_2$$

It forms hydrogen peroxide on distillation with dilute sulphuric acid.

$$H_4SO_5+H_2O+(H_2SO_4) \longrightarrow H_2SO_4+H_2O+(H_2SO_4)$$

It is a strong oxidizing agent.

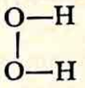
$$2KI+H_2SO_5 \longrightarrow K_2SO_4+H_2O+I_2$$

It oxidizes aniline to aniline black.

Its salts are usually unstable and have not been isolated in pure state.

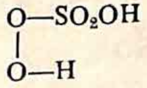
Peroxide. A compound with oxygen in the —1 oxidation state is called a peroxide.

Persulphuric acids. Two peroxo acids of sulphur are well known. They are permonosulphric acid (Caro's acid, H_2SO_5) and perdisulphuric acid (Marshall's acid, $H_2S_2O_8$). These acids are derived from hydrogen peroxide by the replacement of one or both hydrogen atoms by sulphonic groups:



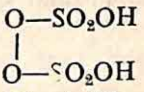
$$\begin{array}{l} O-H \\ | \\ O-H \end{array}$$

Hydrogen peroxide



$$\begin{array}{l} O-SO_2OH \\ | \\ O-H \end{array}$$

Caro's acid



$$\begin{array}{l} O-SO_2OH \\ | \\ O-SO_2OH \end{array}$$

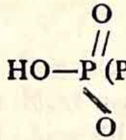
Marshall's acid

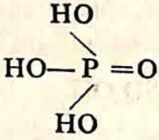
Phosphatic slag. Thomas or Basic slag is obtained as a by-product in the manufacture of steel and is probably a double salt of tricalcium phosphate and calcium silicate. It is soluble in dilute citric and carbonic acids.

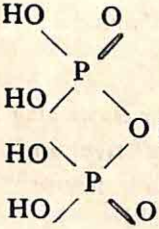
In the presence of salts and carbon dioxide it dissolves in water hence it dissolves in soil water and is taken by the plants in the form of solution through their roots. It is crushed to a fine powder and added to the soil. In the soil it decomposes slowly and supplies necessary phosphoric acid to the soil over a long period.

Phosphor. A substance that can convert absorbed energy into radiation, exhibits luminescence. Most inorganic substances of this kind are phosphor crystals. Their luminescence depends on the presence of small amounts (up to 0.001 per cent) of cation impurities, e.g. traces of copper activate fluorescence of zinc sulphide. Inorganic phosphors are used in luminescent lamps, electron-beam tubes, screens for roentgenoscopy, as indicators of radiation. Organic phosphors are employed to prepare bright phosphorescent pigments, luminescent materials; in chemistry, biology, medicine, criminology as analytical detectors of high sensitivity.

Phosphoric acids.

Metaphosphoric acid  $(P_2O_5+H_2O \xrightarrow{\text{in cold}} 2HPO_3)$;

Orthophosphoric acid  $(HPO_3+H_2O \xrightarrow{\text{reflux}} H_3PO_4)$;

Pyrophosphoric acid  $(2H_3PO_4 \xrightarrow{475\ K} H_4P_2O_7+H_2O)$

Orthophosphoric or merely phosphoric acid is applied more widely than the meta and pyro-forms; it is made from calcium phosphate rocks in industry:

$$Ca_3(PO_4)_2+3H_2SO_4 \rightarrow 3CaSO_4+2H_3PO_4$$

It is used in the manufacture of fertilizers, in the food and textile industries, and in medicine. Its salts, orthophosphates or phosphates, also have important practical applications (fertilizers, components of enamels, glasses).

Phosphorous acids. They are:

H_3PO_3	Orthophosphorous acid (or phosphorous acid)
$H_4P_2O_5$	Pyrophosphorous acid
$(HPO_2)_n$	Metaphosphorous acid

Orthophosphorous acid is obtained by the hydrolysis of phosphorous oxide.

$$P_4O_6+6H_2 \longrightarrow 4H_3PO_3$$

All the phosphorous acids contain P—H bonds and are reduing in character. Both the ortho and pyrophosporous acids are dibasic (contain two OH groups).

Phosphorus [Greek *phosphoros*, bringer of light] **P**. A Gruop VS element of the 3rd period of the Periodic Table of Elements, atomic number 15, atomic mass 30.9738, one stable isotope ^{31}P. Discovered (1669) by alchemist Brand. Essential to animal and plant life.

Properties A non-meltalic element existing in several allotropic forms (red, white). The most reative form is white phosphorus; it ignites, spontaneously in the air and for that reason is stored under water, poisonous, exhibits phosphorescence (hence the name of the element). Phosphorus combines directly with halogens, oxygen, sulphur and metals. The oxidation states in compounds +5 (P_2O_5), +3 (P_2O_3) and —3 (PH_3).

Occurrence Phosphate rock, apatite.

Manufacture By reducing phosphate minerals with coke.

$$Ca_3(PO_4)_2+3SiO_2+5C \rightarrow 3CaSiO_3+2P+5CO$$

Uses In pyrotechnics, in the manufacture of matches, as a deoxidizer in metallurgy, as an alloying element. Certain phosphides are semiconductors (GaP, InP, etc.). Phosphoric anhydride is employed as a drying agent. The most important compounds of phosphorus are phosphoric acid derivatives and phosphorus-containing fertilizers.

Organophosphorus derivatives are widely applied as insecticides.

Phosphorus cycle. Phosphous is also an important element required by plants and animal although in small quantities. Plants assimilate phosphorus from soil where it is present as phosphates and animals get it in the from of food. The plants and animals return the phosphorus to the soil after they die and decay. But the cultivated soil loses its phosphorus from year to year. This deficiency is made up by the addition of phosphatic manures to the soil. Thus a cycle of changes is repeated by means of which the circulation of phosphorus continues in nature which is known as phosphorus cycle.

Phosphorus fertilizers. Mineral fertilizers containing phosphorus. e.g. superphosphate, ammophos, potassium ortho and meta-phosphates, precipitated calcium phosphate, Thomas slag, etc. Made from phosphate rock, apatite.

Phosphorus halides. Phosphorus forms tri-halides with all the halogens. The tetra-halides are formed by fluorine and iodine, while pentahalides are formed by all the halogens eacept iodine. Phosphorus also forms mixed halogen derivatives, e.g. PF_2Cl, PF_2Br, $PFCl_2$ and $PFBr_2$.

Phosphorus oxides. Phosphorus forms three important oxides.

Phosphorus trioxide	$P_2O_3(P_4O_6)$
Phosphorus tetroxide	$P_2O_4(P_4O_8)$
Phosphorus pentoxide	$P_2O_5(P_4O_{10})$

Apart from these oxides P_4O_7 and P_4O_9 are also known.

Phosphous hydrides. Phosphorus forms many hydrides such as PH_3, P_2H_4, P_5H_2, P_9H_2, etc. Bul PH_3 (phosphine) is the most important which is gas P_2H_4 (diphosphine) is a liquid and other hydrides are solids.

Phosphorus oxoacids. Important oxoacids of phosphorus are given below:

Oxoacid of Phosporus	*Oxidation state of phosphorus*
Hypophosphorous acid, H_3PO_2	+1
Orthophosphorous acid, H_3PO_3	+3
Hypophosphoric acid, $H_4P_2O_6$	+4
Orthophosphoric acid, H_3PO_4	+5
Pyrophosphoric acid, $H_4P_2O_7$	+5
Metaphosphoric acid, $(HPO_3)_n$	+5
Peroxophosphoric acids, H_3PO_5 and $H_4P_2O_8$	—

Phosphorus oxychloride, $POCl_3$. It is obtained by the action of water or weak acids on phosphorus pentachloride.

$$PCl_5+H_2O \longrightarrow POCl_3+2HCl$$
$$PCl_5+H_2C_2O_4 \longrightarrow POCl_2+HCl+CO_2+CO$$
$$3PCl_5+2H_3BO_3 \longrightarrow 3POCl_3+6HCl+B_2O_3$$

It is a colourless liquid with pungent smell (b.p. 380 K). It is readily hydrolysed by water.

$$POCl_3+3H_2O \longrightarrow H_3PO_4+3HCl$$

Phosphorus pentachloride, PCl_5. It is prepared by the combination of phosphorus trichloride and chlorine.

$$PCl_3+Cl_2 \longrightarrow PCl_5$$

Phosphorus trichloride is introduced dropwise in a flask kept in freezing mixture and a current of dry chlorine is passed into it After the reaction excess of chlorine is removed by passing carbon dioxide and the flask is then closed.

It is a colourless or light yellow coloured solid with pungent smell. It sublimes at 373 K and melts at 318 K under pressure.

It dissociates at 775 K as:

$$PCl_5 \longrightarrow PCl_3+Cl_2$$

The oxygen atom of an aldehyde, ketone, a sulphur dioxide, etc. is replaced by two chlorine atoms when they react with it.

$$CH_3CHO+PCl_5 \longrightarrow CH_3CHCl_2+POCl_3$$
$$CH_2COCH_3+PCl_5 \longrightarrow CH_3CCl_2CH_3+POCl_3$$
$$SO_2+PCl_5 \longrightarrow SOCl_2+POCl_3$$

It reacts with fine powdered metal to form metal chloride.

$$2Ag+PCl_5 \longrightarrow 2AgCl+PCl_3$$
$$2Cu+PCl_5 \longrightarrow Cu_2Cl_2+PCl_3$$

It is used for the replacement of hydroxyl group by chlorine.

Phosphorus pentafluoride PF_5. It is prepared by heating calcium fluoride with phosphorus pentoxide.

$$10CaF_2+P_4O_{10} \longrightarrow 10CaO+4PF_5$$

It is a clourless gas and gives fumes of POF_3 in air. It is hydrolysed by water as:

$$PF_5+4H_2O \longrightarrow H_3PO_4+5HF$$

Phosphorus trichloride, PCl_3 It is prepared by passing dry chlorine over heated white phosphorus. The trichloride distills over and collected.

$$P_4 + 6Cl_2 \longrightarrow 4PCl_3$$

It can also be obtained by the action of phosphorus on thionyl chloride.

$$P_4 + 8SOCl_2 \longrightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$$

It is a colourless, mobile liquid (b.p.337 K. f.p. 161.5 K, sp. gr. 1.6) with strong pungent smell. It forms fumes in the moist air.

Phosphorus trifluoride, PF_3 It is produced by the fluorination of phosphorus compounds.

$$AsF_3 + PCl_3 \longrightarrow AsCl_3 + PF_3$$
$$3ZnF_2 + 2PBr_3 \longrightarrow 3ZnBr_2 + 2PF_3$$
$$3PbF_2 + Cu_3P_2 \longrightarrow 3Cu + 3Pb + 2PF_3$$

It is a colourless gas and hydrolysed by water

$$2PF_3 + 3H_2O \longrightarrow 2HF + H_3PO_3 + \underset{\text{Hydrofluophosphoric acid}}{HPF_4}$$

Phosphorus trioxide, P_4O_6. It is prepared by heating phosphorus in a limited quantity of oxygen or air.

$$P_4 + 3O_2 \longrightarrow P_4O_6$$

It is purified by distillation or dissolution in organic solvents after conversion of unreacted phosphorus to red phosphorus by exposure to mercury arc (i.e. ultraviolet light). Red phosphorus is insoluble in organic solvents. Thus phosphorus trioxide is obtained in pure state.

It is a crystalline solid with strong garlic smell and sharp sour taste (b.p. 446 K. m.p. 295.5 K). Its vapour density (110) corresponds to the molecular formula P_4O_6.

It is soluble in organic solvents and poisonous in nature.

It decomposes on heating at 485 K.

$$4P_4O_6 \longrightarrow 3P_4O_8 + P_4$$

It reacts with water as:

$$P_4O_6+6H_2O \longrightarrow 4H_3PO_3$$
(cold)

$$P_4O_6+6H_2O \longrightarrow 3H_3PO_4+PH_3$$
(hot)

The vapour density of phosphorus trioxide is 110 which corresponds to the molecular formula P_4O_6. Its structure is connected with the structure of P_4 molecule which is tetrahedral and phosphorus atoms are situated at the corners. The six oxygen atoms are situated slightly shifted from six planes. The P—O distance is 1.638 Å which is shorter than expected value for single bond (1.84Å). This is due to the existance of considerable double bond character in the P—O bonds because of the formation of a pπ-dπ dative bond with oxygen donor.

Photochemical reaction. A reaction which involves the absorption of electromagnetic radiation is called a photochemical reaction. Generally in at least one step in the mechanism the formation of the activated complex can occur only if a photon of radiation is absorbed. Some examples of photochemical reactions are photolysis reactions and photosynthesis.

Photochemicals. These are produced by a set of complicated reactions starting with the absorption of radiation by nitrogen dioxide. The gas absorbs sunlight in the blue and near UV region of the spectrum and decomposes into nitric oxide and oxygen. This is followed by other reactions when pollutants like ozone, aldehydes ketones, peroxyacyl nitrates (PAN), etc., are produced.

$$NO_2+h\nu \rightarrow O+NO$$

$$O_2+O \rightarrow O_3 \text{ (ozone)}$$

$$O_3+NO \rightarrow NO_2+O_2$$

$$R\text{H (hydrocarbon)}+O \rightarrow RO^\circ$$

$$RO^\circ+O_2 \rightarrow RO^\circ_3$$

$$RO^\circ_3+R\text{H} \rightarrow \text{Aldehydes}+\text{Ketones}$$

$$RO^\circ_3+NO \rightarrow RO_2+NO^\circ_2$$

$$RO^\circ_3+O_2 \rightarrow RO_2+O^\circ_3$$

$$RO^\circ_2+NO_2 \rightarrow \text{Peroxyacyl nitrates (PAN)}$$

These photochemical pollutants (particularly O_3) are powerful eye irritants and cause bronchial irritation. The aerosols formed during the course of reaction reduce visibility in atmosphere and produce what is known as 'photochemical smog'.

Some of the photochemicals are able to affect the respiratory systems adversly to effect the athletic pertormance of human beings and are damaging the leafy crops such as spinach and letuce.

Photoelectric effect. Light striking the surface of some substances will cause the emission of electrons from the substance. This effect, the photoelectric effect, is pronounced for cesium metal and for some of its alloys and compounds.

Photolysis. In a photolysis reaction a photon of radiant energy is absorbed by a molecule which subsequently splits into two parts.

Plant nutrients. Plants for their normal and healthy growth require about sixteen elements called plant nutrients. Out of these three, namely carbon, hydrogen and oxygen are derived from air and water. The remaining thirteen elements are supplied by the soil. These may be classified as follows;

Primary neutrients Nitrogen, phosphorus and potassium are consumed in large quantities by the plants and they are, therefore, called primary nutrients.

Secondary nutrients These are calcium, magnesium and phosphorus which come next in importance to the primary nutrients for plant growth.

Micronutrients These include zinc, boron, copper, manganese, molybdenum, chlorine and iron. These are required by plants only in minute quantities.

Platinised asbestos. It is prepared by soaking asbestos fibre in a solution of chloroplatinic acid and then heating to 775 K. On heating chloroplatinic acid decomposes into finely divided platinum which is distributed throughout the asbestos fibre. The asbestos fibre impregnated with finely divided platinum is known as platinised asbestos and was used as catalyst in the manufacture of sulphuric acid by the Contact Process.

Platinum. [Spanish *plata* silver] Pt. A 5d element of the 6th period of the Periodic Table of Elements, atomic number 73, atomic mass 195.09. The most abundant of platinum family metals.

Properties A silvery white metal, ductile, malleable. At room temperature reacts only with aqua regia and bromine. The usual oxidation states in compounds are +2, +4. Has many valuable properties such as chemical stability, high melting point, the constancy of mass at low and high temperatures, the ability to accelerate chemical reaction. Forms many complex compounds.

Occurrence Mainly found in the free state.

Uses In the manufacture of chemical equipment for work in aggressive media, as a catalyst, in electrical devices, in jewelry. Platinum electrodes are employed in various fields of the chemical industry. Used in the pure form and as alloy component.

Platinum black. It is a velvety black powder obtained when platinum is precipitated from solution of its tetrachloride by reducing agents, like sodium formate, glucose, etc. This is extensively used as catalyst.

Platinum metals. These are ruthenium (Ru), rhodium (Rh) palladium (Pd) (the lighter platinum metals) and osmium (Os), iridium (Ir), and platinum (Pt) (the heavier platinum metals). Occur in nature together with platinum. All platinum metals are stable towards chemical actions.

Plutonium (At. No. 94). The second transuranic element was later named plutonium after the planet pluto. It has two isotopes ${}^{238}_{94}\mathrm{Pu}$ and ${}^{239}_{94}\mathrm{Pu}$, the later being most important. It has been discovered by Seaborg and co-workers as decay product of neptunium-239.

$${}^{238}_{93}\mathrm{Np} \longrightarrow {}^{238}_{94}\mathrm{Pu} + e^{-} \text{ (half-life 90 years)}$$

$${}^{239}_{93}\mathrm{Np} \longrightarrow {}^{239}_{94}\mathrm{Pu} + e^{-} \text{ (half-life of } 2.4 \times 10^{4} \text{ years)}$$

Plutonium-239 is fissonable with slow neutrons which places it in the same class with uranium-235 as a nuclear fuel.

Pollutant. Pollutant may be defined as a constituent in the wrong amount at the wrong place or at the wrong time.

An interesting axample is that nitrogen and phosphorus are essential nutrients for living organisms and are used in crops to increase their production but they can cause pollution in lakes and rivers by increasing algae growth.

Pollutant has adverse effect on environment, animal and plant life. This has weakened plant and animal population and in some cases this has proved even lethal.

Polonium (After Poland, the native land of Marie Curie) **Po**. A Group VIA radioactive element of the 6th period of the Periodic Table of Elements, atomic number 84, discovered in pitchblende by Pierre and Marie Curie in 1898, The longest-lived natural isotope, ^{210}Po ($t^1/_2$ 138 days), undergoes alpha-decay.

Properties A soft silvery white metal, the oxidation states in compounds —2, +2, +4, +6; resembles tellurium and bismuth in its chemical properties.

Uses In neutron sources, in radiochemistry to study chemical transformations under alpha-irradiation, in the manufacture of atomic batteries.

Polydentate ligands. When a ligand has two or more donor atoms which may simultaneously co-ordinate to a metal atom, it is termed as a multi or polydentate ligand. Depending upon the number of donor sites, these ligands may be referred to as bidentate (two donor atoms), tridentate (three donor atoms), tetradentate (four donor atoms) and so on.

Examples of bidentate ligands are 2,2′-dipyridyl, oxalato dimethylglyoxime, ethylenediamine, etc. Examples of tridentate ligands are diethylene triamine and iminodiacetic acid anion.

In ethylenediamine, $H_2N-CH_2—CH_2-NH_2$ the N atoms of the two amino groups can act as electron donors at the same time. Therefore, co-ordinate bond could be formed by both of them. This is a bidentate ligand.

Polysulphides. The sulphides of alkali metals, alkaline earth metals, and ammonium dissolve free sulphur to form polysulphides, e.g. Na_2S_2, Na_2S_3, $Na_2.S_5$ $(NH_4)_2$ S, etc. These are yellow in colour. Ammonium polysulphide is also known as yellow ammonium sulphide and used as a laboratory reagent in the separation of IIA and IIB group cations. The sulphides of As Sb and Sn are soluble in yellow ammonium sulphide.

$$M_2S_3+3(NH_4)_2S_2 \longrightarrow 2(NH_4)_3MS_4+S \qquad (M=\text{As, Sb})$$
$$SnS+(NH_4)_2S_2 \longrightarrow (NH_4)_2SnS_2$$

A solution of calcium polysulphide is used in agriculture as fungicide and insecticide.

Polythionic acids. Polythionic acids are unstable acids and decompose into sulphur dioxide and sulphates. The polythionates are stable and can be obtained by the reduction of thionates are stable and can be obtained by the reduction of thiosulphate solution with sulphur dioxide in the presence of arsenic trioxide.

The polythionates are oxidized by oxidizing agents and are reduced with alkali sulphides, e.g.

$$Na_2S_3O_6+2H_2O+4(O) \longrightarrow Na_2SO_4+2H_2SO_4$$
$$Na_2S_4O_6+3H_2O+7(O) \longrightarrow Na_2SO_4+3H_2SO_4$$
$$Na_3S_3O_6+Na_2S \longrightarrow 2Na_2S_3O_3$$
$$Na_2S_4O_6+Na_3S \longrightarrow 2Na_5S_2O_3+S$$

Tetrathionates give thiosulphates and trithionates on reduction with alkali sulphites.

$$Na_2S_4O_6+Na_2SO_3 \longrightarrow Na_2S_2O_3+Na_2S_3O_6$$

Portland cement. Portland cement is the most important building material. In 1824 Joseph Aspidin first of all introduced it in England. He prepared a material by calcining limestone and clay. It was mixed with water and allowed to stand for few hours when it became a hard stone-like substance very similar to Portland rock, a famous bulding stone of England, and named as Portland cement.

The average composition of cement is:

CaO	50-60%	MgO	2-3%
SiO_2	20-22%	Fe_2O_3	2-5%
Al_2O_3	7-10%	SO_3	1-2%

Cement free from iron is white but hard to burn. If lime (CaO) content is lower then the strength of cement is low and sets quickly. If more lime is there that causes cracks after setting. Excess of silica gives slow setting cement. Excess of aluminia produces quick setting cement.

It is a dirty greenish, heavy powder which is essentially a mixture of tricalcum silicate, $3CaOSiO_2$, dicalcium silicate, $2CaO.SiO_2$ tricalcium aluminate, $3CaO.Al_2O_2$ and tetracalcium aluminoferrate, $4CaO.Al_2O_3.FeO_3$. These compounds make about 90% of the cement. Out of these $3CaO. SiO_2$ is the most important.

The raw materials for the manufacture of cement are:
Limestone (which provides lime) and
Clay (which provides alumina).

Positron. A positron is a particle which is virtually identical to the electron except that its charge is positive. It is one of a collection of antiparticles which includes an antiproton and even an antinutron. Positrons are typically emitted by nuclei below the trough of stability.

Potash. (Dutch *pot* a pot+*asch*, **ash**: so called from the original method of manufacture) A technical term for potassium carbonate, K_2CO_3

Potasium [see *potash*] **K**. A Group IA element of the 4th period of the Periodic Table of Elements, atomic number 19, atomic mass 39 102. Was first isolated by Davy in 1807 by electrolysis of KOH.

Properties A silvery white very soft metal, easy to cut by a knife. The oxidation state in compounds +1. Very reactive, is rapidly oxidized in the air, reacts vigorously with halogens to give the corresponding salts. Combines with sulphur with the formation of potassium sulphide, K_2S. Violently reacts with water and acids replacing hydrogen. Readily reacts with many organic substances such as alcohol (forms potassium alkoxides), acetylene (in the cold to give KHC_2).

Occurrence Found in many rocks; the most important ones are feldspar and mica. Contained in sea water. The main minerals are sylvite, KCI, carnallite, $KCl.MgCl_2.6H_2O$ and kainite, $KCl.MgSO_4,3H_2O$.

Preparation By reducing molten potassium hydroxide or potassium chloride with sodium:

$$KOH + Na \rightarrow K + NaOH$$
$$KCl + Na \rightarrow K + NaCl$$

Uses Potassium metal is used in the manufacture of potassium peroxide, K_2O_2, for oxygen-generating gas masks (releases oxygen under the action of moist air); as catalyst in the manufacture of some kinds of rubber. Potassium-sodium alloy is used as coolant in nuclear devices and as a reducing agent in the manufacture of certain metals, e.g. titanium. Potassium salts (KCl, etc.) are soil fertilizers.

Potassium carbonate. Ammonia soda (Solvay) process cannot be employed to manufacture potassium carbonate because potassium bicarbonate is too soluble to be precipitated. It can be prepared by passing carbon dioxide through a solution of potassium hydroxide when bicarbonate obtained is ignited to the salt.

$$KOH + CO_2 \longrightarrow KHCO_3$$
$$2KHCO_3 \xrightarrow{\text{ignite}} K_2CO_3 + CO_2 + H_2O$$

It finds use in the manufacture of hard glass, soaps and many other potassium salts. In the laboratory, it is used as a drying agent and also as a constituent of fusion mixture.

Potassium chlorate **(Bertholett's salt)** $KClO_3$. Potassium salt of chloric acid. Prepared by heating potassium hypochlorite:

$$3KClO \rightarrow KClO_3 + 2KCl$$

or by bubbling chlorine through a hot solution of potassium hydroxide.

$$6KOH + 3Cl_2 \rightarrow 5KCl + KClO_3 + 3H_2O$$

An oxidizing agent. Used in the manufacture of matches, in pyrotechnics, as source of oxygen in laboratories.

Potassium compounds. Potassium carbonate (potash), K_2CO_3, used in the manufacture of glass and soap, as fertilizer, in the manufacture of potassium salts. Potassium nitrate (nitre, saltpetre), KNO_3 a fertilizer, also used in pyrotechnics, as food preservative, in the manufacture of glass, etc. Potassium permanganate, $KMnO_4$ a strong oxidizing agent, used in the organic synthesis, in medicine, in the analytical chemistry. Potassium sulphate, K_2SO_4 forms numerous double salts, e.g. alum, is used as fertilizer, and in the manufacture of alum and other potassium salts. Potassium chloride, KCl used as fertilizer and in the manufacture of KOH and various potassium salts. Potassium chromate, K_2CrO_4 used in the analytical chemistry. Potassium dichromate, $K_2Cr_2O_7$ used in the manufacture of matches, in pyrotechnics, photography, and in the analytical chemistry. Potassium cyanide, KCN exceedingly poisonous, used in galvano-processes, for nitriding steel, for extraction of gold and silver from their ores.

Potassium hydroxide (caustic potash) **KOH.**

Properties Colourless deliquescent crystals; a strong alkali in aqueous solutions.

Manufacture By electrolysis of potassium chloride solutions.

Uses In the manufacture of liquid soaps and various potassium compounds.

Potassium perchlorate, $KClO_4$. It is prepared by heating (above 645 K) or by the electrolytic oxidation of potassium chlorate.

$$4KClO_3 \longrightarrow KCl + 3KClO_4$$
$$KClO_3 + H_2O \longrightarrow KClO_4 + H_2$$

It is a colourless crystalline solid, sparingly soluble in water. On heating it decomposes to yield oxygen.

$$KClO_4 \longrightarrow KCl + 2O_2$$

It reacts with hot concentrated sulphuric acid to form perchloric acid.

$$KClO_4 + H_2SO_4 \longrightarrow KHSO_4 + HClO_4$$

It is used in the manufacture of explosives and in match industry.

Praseodymium. It is a soft ductile malleable silvery element of the lanthanide series of metals. It occurs in association with other lanthanides. Praseodymium is used in several alloys, as a catalyst, and in compound form in carbon-arc search-lights, etc. and in the glass and enamel industries.

Symbol Pr; m.p. 1204 K; b.p. 3485 K.

Precipitation From Homogeneous Solution (PFHS). One of the major objectives in quantitative precipitation in gravimetric analysis is the separation of a pure solid phase. This may be achieved by precipitation from solution in which the supersaturation is as low as possible. The importance of small degree of supersaturation was, for the first time, indicated by van Weiman—when the supersaturation is small fewer nuclei are initially formed; these nuclei then grow to large aggregates as additional solid phase deposits on them. Then product thus obtained is more easily filtered and is less contaminated by coprecipitation.

It is to maintain small supersaturation that analytical chemists follow the practice of adding a dilute solution of a precipitating reagent slowly and with stirring. Willard and Teng, for example, were able to precipitate 100 mg of Al in exceptionally dense form by adding 0.2 M ammonia solution over a period of several days. The same authors also found that the result could be obtained by in situ generation of OH^- by hydrolysing urea in an hour or less in the presence of Al^{3+}. The obvious practical limit to these expedients are the increased solubility losses in the more dilute solutions and medium of slow addition process. Furthermore, these techniques do not entirely eliminate high supersaturation and rapid precipitation. At the point in solution a new drop of the reagent first makes contact, there is atleast momentarily a high degree of concentration of the reagent. Until stirring disperses the drop there exists a high local supersaturation and consequent rapid formation of the solid. Even with the most efficient working this local effect cannot be eliminated.

"Precipitation from Homogeneous Solution" is an ingenious method for introducing a precipitating reagent in such a way as to avoid the local excesses that accompany mechanical addition of the reagent. The precipitation is caused by slowly generating the reagent throughout the entire solution by means of a suitable chemical reaction. During the process, solvent remains homogeneous with respect to the concentration of ions being precipitated and the reagent: if the generating reaction is slow high supersaturation is avoided and gradual formation of the solid takes places throughout the entire solution.

Since the time this valuable technique was recognized many improvements have been made in its application. The method is no longer confined to getting easily filterable and least contaminated precipitate but has been found useful in the separation of such ions which are otherwise difficult, if not impossible to separate.

Precision. It describes the closeness of approach of replicate results to a common value. Repeated measurements of the same quantity will usually not be identical, but will scatter around some common value. Pricision describes the reproducibility or scatter of a series of measurements of result. Precision may also be defined as the concordance of a series of measurement of the same quantity.

Principal quantum number (n). This quantum number (n) largely determines the energy of the electron according to the expression,

$$E=-\frac{k}{n^2}$$

in which $k=2nm_e e^4/h^2$ (as in Bohr theory).

It also tells the probable distance of the electron from the nucleus (viz. size of the atom). Its values are positive integers as 1, 2, 3 except zero depending upon whether the electron is in the first, second or third principal energy level. The higher the number, the larger the energy possessed by an electron. The energy level represented by the principal quantum number (n) is also known as shell. The K, L, M, N shells corresponding to n numbers 1, 2, 3, 4 respectively may be conveniently regarded as representing series of shells of increasing radius about the nucleus of the atom.

Producer gas. It is a mixture of carbon monoxide (25-30%), nitrogen (50-55%), and hydrogen (10-15%), prepared by passing air with a little steam through a thick layer of white-hot coke in a furnace or 'producer'. The gas is used while still hot to prevent heat loss and finds uses in industrial heating, for example the firing of retorts and in glass furnaces.

Promethium. It is a radioactive element of the lanthanide series of metals. It is not found naturally on earth but can be produced artificially by the fission of uranium. Possible uses involve its radioactive properties.

Symbol Pm; m.p. 1441 K (approx.); b.p. 2733 C (approx.); stablest isotope ^{145}Pm (half-life 18 years).

Protactinium [Greek *protos*, first+actinium] **Pa.** A radioactive f block element of the 7th period of the Periodic Tabie of Elements, atomic number 91, an actinide, discovered by Hahn and Meitner (1918) (Fajans and Goring are said to be co-discoverers). Occurs in nature as ^{231}Pa ($t_{1/2}$= 34300 years), precedes actinium in the actinium radioactive series, $^{231}\text{Pa} \rightarrow {}^{227}\text{Ac}$, whence derives its name.

Properties White-grey metal; the oxidations states +2, +3, +4, +5. Protactinium compounds are readily hydrolyzed and adsorbed from solutions on vessel walls.

Protonic and aprotic solvents. Solvents from which protons (i.e. H^+ ions) can be derived are called protonic solvents. H_2O NH_3, HF, etc. are the best examples of protonic solvents. Solvents from which proton cannot be ordinarily derived are called aprotic solvents. Examples are CCl_4, C_6H_6, etc.

The main drawback of this type of classification is that it has no practical utility in non acid-base behaviour.

Pseudohalogens. Pseudohalogens (also called halogenides) are complex molecules which behave like halogens. Some examples are:

Cyanogen, $(CN)_2$
Oxycyanogen, $(OCN)_2$
Thiocyanogen, $(SCN)_2$
Selenocyanogen, $(SeCN)_2$
Tellurocyonogen, $(TeCN)_2$
Azidocarbondisulphide, $(SCSN_3)_2$.

The anions of the pseudohalogens give reactions similar to those given by halide ions. These ions are called pseudohalides. For example:

Cyanide, CN^-
Cyanate, OCN^-
Thiocyanate, SCN^-
Selenocyanate, $SeCN^-$
Tellurocyanate, $TeCN^-$
Azide, N_3^-.

The pseudohalide CN^- forms HCN (like halogens X form HX), insoluble salts with Ag^+, Pb^{2+} and Hg_2^{2+} (like Cl^- forms AgCl, $PbCl_2$ and Hg_2Cl_2) and complex ions like $[Cu(CN)_4^{2-}$, $Co(CN)_6^{3-}]$, etc. similar to $CuCl_4^{2-}$, $CoCl_6^{3-}$, etcr The CN^- can be oxidized to $(CN)_2$. AgCN is insoluble in wate. but soluble in ammonia (similar to the behaviour to AgCl). Like interhalogens formed by halogens, interpseudohalogens CICN, BrCN and ICN are also known.

Pseudohalogens can be prepared by the following methods:

Reaction of CN^- with Cu^{2+} salt gives cyanogen.

$$2Cu^{2+}+4CN^- \longrightarrow 2CuCN+(CN)_2$$

Electrolysis of potassium cyanate, KOCN in methyl alcohol gives oxycyanogen.

Thiocyanogen can be prepared by the reaction of a halogen with AgSCN.

$$2AgSCN+X_2 \longrightarrow 2AgX+(SCN)_2$$

Reaction of iodine with AgSeCN gives selenocyanogen.

$$2AgSeCN+I_2 \longrightarrow 2AgI+(SeCN)_2$$

Electrolysis of potassium tellurocyanate (KTeCN)in methyl alcohol gives tellurocyanogen.

Azidorcarbondisulphide is obtained by the oxidation of $KSCSN_3$ with chlorine or hydrogen peroxide.

Pyrophosphoric acid, $H_4P_2O_7$. It is obtained by heating orthophosphoric acid at 525 K or by heating equimolar mixture of ortho-and metaphosphoric acids at 375 K

$$2H_3PO_4 \xrightarrow{525\text{ K}} H_4P_2O_7+H_2O$$

$$H_3PO_4+HPO_3 \xrightarrow{375\text{ K}} H_4P_2O_7$$

It is a colourless crystalline solid (m.p. 334 K), On heating it gives metaphosphoric acid.

$$H_4P_2O_7 \xrightarrow{875\text{ K}} 2HPO_3+H_2O$$

It is a tetrabasic acid ($K_1=1\times10^{-1}$, $K_2=3.2\times10^{-2}$, $K_3=1.7\times10^{-6}$ and $K_4-6.0\times10^{-9}$).

But only two series of salts are commonly known, the diacid salts, $Na_2H_2P_2O_7$ and normal salts, $Na_4P_2O_7$

Q

Quantum numbers. Since Schrodinger wave equation is the equation of three-dimensional wave, in which the values of m and V are known, the mathematical solution of the wave equation gives three values of E for acceptable value of ψ. These values are related to one another through whole numbers. These values termed quantum numbers as n, l and m are called principal, azimuthal and magnetic quantum numbers respectively. These three quantum numbers together with fourth spin quantum number (m_s) describe fully the allowed energies and general behaviour of an electron. Thus quantum numbers are the numbers which determine energy of the electron, the angular momentum and shape of the electron cloud, the orientation of the electron cloud and spin of the electron.

The three quantum numbers the principle (n), azimuthal (l) and the magnetic (m) are derived directly from the wave equation whereas the fourth quantum number, spin arises from the direction of the spin of the electron. These four quantum numbers are like labels used to describe completely the energy state of an electron.

Quartz. A mineral, one of the most abundant forms of silica, SiO_2, Hardness 7. Varieties: colourless transparent (rock crystal), violet (amethyst), smoky (cairngorm or smoky quartz), black (morion), yellow (citrine).

Properties Vitreous lustre, chemically stable. Practically insoluble in water and acids at 298 K, less stable to the action of alkalis, especially at elevated temperatures.

Source From quartz sand, sandstone, quarzite, and quartz veins.

Uses In the glass and building industries. Admixtures of quartz increase strength and refractoriness of porcelain. Also used as an abrasive (grindstones, grinding wheels), Transparent quartz is used in electrical and radio engineering.

Quartzite (quartz rock). A rock composed almost wholly (by 95 to 98 per cent) of quartz grains. Used as tower packings in the manufacture of H_2SO_4, HNO_3, HCl, and as a material for refractory bricks (silica bricks).

R

Radiation. Radiation is a broad term encompassing both electromagnetic waves (radio, radar, infrared, visible, ultraviolet, X ray, gamma ray, etc.) and particles such as those which result from nuclear disintegration (α particles, β particles neutrons, etc.), Radialion can also be classed as ionizing (with enough energy to remove electrons from atoms or molecules) or nonionizing.

Radiometric analysis. The detection of radioactive isotopes in a given sample based on the determination of their half-lives and the type and energy of emltted radiation.

Radium [Laint *radius*, a ray] **Ra**. A Group IIA radiocative element of the 7th period of the Periodic Table of Elements, atomic number 88, discovered in 1898 by the Curies in pitchblende. The longest lived isotope is ^{226}Ra ($t_{1/2}=1617$ years), a member of the ^{238}U series, occurs in all uranium ores. The ^{226}Ra isotope decays with the emission of alpha rays and formation of radon, an inert gas: $^{226}Ra \rightarrow {}^{222}Rn$.

Properties A silvery white metal, resembles barium in its chemical properties, the oxidation state in compounds +2. Radium salts are less soluble than the corresponding barium salts.

Occurrence In uranium ores, in many natural waters.

Uses As a source of alpha particles in radium-beryllium neutron sources (berylium emits neutrons under alpha irradiation), as a source of gamma rays in gamma radiography, in the manufacture of luminous paints, in medicine (radiotherapy, treatment of skin diseases, cancer).

Radon. [radium + on, as in neon, etc.] **Rn.** A Zero Group element of the 6th period of the Periodic Table of Elements, atomic number 86, an inert (noble) gas. Discovered in 1900 by Dorn. The longest lived isotope is ^{222}Rn ($t_{1/2}$=3.8 days), formed in alpha decay of ^{226}Ra, whence the name of the element (earlier called radium emanation, Em). Used in science and medicine (e.g. radon baths).

Redox Titrations. Redox, i.e. reduction-oxidation titrations can be conducted using reagents which behave as reducing and oxidizing reagents. These reagents are usually coloured in the oxidized or reduced from but of significantly different colour (or even colourless) in the other state. For example, potassium permagnate is purple in its oxidized form, but its reduced product, i.e. manganese (II) ion is almost colourless.

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

In some cases, the colour change is not distict to ensure accuracy. For example the iodine is brown in solution, the iodine ion is colourless.

$$I_2 + 2e^- \longrightarrow 2I^-$$

As the iodine is reduced, the colour fades to a pale yellow which is difficult to distinguish from the colourless iodide ion. If starch is added, an intenee blue colour appears in the presence of even a trace of iodine. It is colourless in the absence of Iodine.

Redox titrations involve reactions in which a change in oxidation number takes place and are used to estimate the amount of an oxidizing agent or that of a reducing agent from their solutions. In these reactions oxidation and reduction take place simultaneously. If one substance is oxidized then the other is reduced.

Representative elements. These element are characterized by atoms with outer level incomplete and inner levels filled to their capacity. The electronic configurations in the outer shell of the atom of these elements include structures ns^1, ns^2 and ns^2np^1 to ns^2np^5. The groups of the periodic table in which these elements fall are IA, IIA, IIIA, IVA VA, VIA and VIIA. These groups are also known as main groups of the periodic table. All the non-metals have this type of electronic configuration.

Resonance. It is the description of electronic structure of molcecule by means of several schemes of pairing of electrons, with features of each scheme contributing in the description.

For example, carbon dioxide molecule is usually represented as:

$$:\ddot{O}:C::\ddot{O}: \quad \text{or} \quad O{=}C{=}O$$

I

Though the structure I can explain many properties of the molecule, it fails to explain all of its known properties. The actual carbon-oxygen bond length in CO_2 molecule is 1.15 Å against 1.22 Å expected from the structure I. Also, actual heat of formation of CO_2 is 1590 kJ mol^{-1} though the structure I suggests it to 1464 kJ mol^{-1}. The descrepancies can be accounted for by considering the contributing structures II and III for the moleule.

$$:\underset{..}{\ddot{O}}:C::\overset{+}{O}: \quad \text{or} \quad \overset{-}{O}{-}C{\equiv}\overset{+}{O}$$

II

$$:\overset{+}{O}::C:\underset{..}{\ddot{O}}: \quad \text{or} \quad \overset{+}{O}{\equiv}C{-}\overset{-}{O}$$

III

Although the octet rule permits all the three structure (I-III) for CO_2 yet none of them accounts for all the known properties of the molecule. Hence none of these structures is the real structure of the molecule. The true structure is hypothetical and resembles the structure I, II and III but it is different. This new and different structure is known as *resonance hybrid*. The structures I, II and III which do not represent the true structure of CO_2 but contribute to the hypothertical true structure, i.e. resonance hybrid are called *canonical structures* (or contributing structures). The resonance hybrid is shown by putting double headed arrow (⟷) between various resonating forms as shown in case of CO_2.

$$\underset{\text{I}}{O=C=O} \longleftrightarrow \underset{\text{II}}{\overset{-}{O}-C\equiv\overset{+}{O}} \longleftrightarrow \underset{\text{III}}{\overset{+}{O}\equiv C-\overset{-}{O}}$$

Rhenium. The element Rhenium was discovered by Noddack and Tracke in 1925 after a planned and careful search in possible minerals. This element was suspected to be present only in traces in the minerals of neighbouring elements and, therefore, concentrated to obtain the element in detectable quantities which were prepared by laborious methods. In 1928, these investigators were able to isolate one gram of pure rhenium from 660 kg of molybdenite minerals. Now this metal is available in commercial quantities.

There are no minerals of rhenium. Investigations have shown that silicates, niobates, tungstate and sulphide minerals usually contain trace amounts of the metal. The metal has been found associated with platinum ores. The ores containing rhenium are as follows:

Ore	*Rhenium content in g per tonne*
Molybdenite	21.0
Osmiridium	1.0
Lead selenite	0.8
Gadolinite	1.1
Native platinum	0.1

On roasting of molybdenite, the rhenium present as disulphide is converted into three oxides, Re_2O_7, ReO_3 and ReO_2 which being appreciably volatile go into the gas phase. Thus 75.95 per cent of rhenium passes into the gas phase. Under favourable conditions, these oxides condense in the form of smoke particles and are separated by electrostatic filters or gas washing.

Following methods are employed to bring rhenium into solution phase from the flue dust, concentrated as given above.

Direct leaching with water Re_2O_7, the main rhenium consitituent of the flue dust, being soluble in water yields a solution of rhenium. The residue containing dioxide and trioxide is then treated with dil. HCl or H_2SO_4 to extract 30. 60 per cent of the remaining rhenium.

Leaching with water containing oxidizing agent A suspension of flue dust in water. when reacted with an oxidizing agent like chlorine, bromine or hypochlorite brings about 90 per cent rhenium into solution.

Leaching with water after sintering The flue dust is sintered at about 875 K often being mixed with one and half times its weight of slaked lime. Calcium perrhenate, a readily soluble salt, is formed which is leached with warm water (and after two hours rhenium solution is filered out.

Extraction of rhenium from solution The rhenium solution obtained from the above methods is mainly concentrated and then KCl is added. A crude potassium perrhenate ($KReO_4$) is precipitated. It is to be recrystallized several times before it is obtained in the pure state.

The crude potassium perrhenate is dissolved in boiling water containing H_2SO_4. The solution is filtered off to remove insoluble impurities. On cooling and adding more of KCl to the solution comparatively pure $KReO_4$ is obtained. After repeating the process several times very pure potassium perrhenate is obtained.

Molybdenite mineral contains two to four parts of rhenium in million parts of the ore. This is the most convenient source for the extraction of rhenium. The sulphide mineral is powdered and treated with concentrated HNO_3 at 345 to 355 K which convents molybdenum disulphide into molybdenum trioxide and rhenium to Re_2O_7. The solution is diluted with water and insoluble molybdenum trio·ide, MoO_3 is filtered out. The filtrate is then concentrated by evaporation and treated with conc. H_2SO_4. The sulphuric acid solution is distilled first in steam of CO_2 upto 445 K and finally in hydrogen chloride gas between 445-475 K. The distillate contains rhenium heptoxide, Re_2O_7 with small amounts of molybdeum trioxide. From this distillate rhenium is sparated in the following way:

The distillate containing the two oxides is treated with the solution of oxine or 2,2′-dipyridyl so that molybdenum is completely preciptated as the complex salts. The filtrate is then treated with the solution of nitron acetate so that nitron perrhenate is precipitated. This is filtered out, dried again, and igited to obtain rhenium heptoxide.

Rhenium metal is usully obtained by reducing $KReO_4$ by hydrogen above its melting point.

$$2KReO_4 + 7H_2 \longrightarrow 2Re + 2KOH + 6H_2O$$

Sometimes H_2 at a pressure of 20-100 atmosphers is employed for this purpose. A relativelv low temperaturc of 475 575 K is required.

Elerctodeposition On electrolysing a solution of potassium perrhenate in H_2SO_4, rhenium is deposited at the cathode. Anode is made up of platinum while cathode is of tantalum or graphite. Metal of 99.9 per cent purity is obtained by this method.

High purity rhenium metal is made by the hydrolysis of $ReCl_5$ in aqueous medium to ReO_2 and subsequent reduction of the product with H_2.

Finely divided rhenium is a grey-black powder but the compact metal is white like platinum. Pure rhenium is quite soft and malleable in the compact state. Rhenium melts at 3453 K and boils at about 5803 K. The metal crystallizes with hexagonal close packed structure.

Finely-powdered metal oxidizes easily in air at 423 K. The compact metal is oxidised by oxygen when heated above 1275 K.

$$4Re + 7O_2 \longrightarrow 2Re_2O_7$$

Rhenium metal is direclty attacked by halogens to form halides. Fluorine reacts at 400 K to from the hexafluoride ReF_6, chlorine reacts with rhenium at high temperature to form pentachloride $ReCl_5$ and trichloride $ReCl_3$, while bromine racts with rhenium at 775 K to form tribromide $ReBr_3$. A staeble iodide of rhenium has been obtained in pure state.

$$Re+2F_2 \xrightarrow{400\ K} ReF_6$$

$$2Re+4Cl_2 \xrightarrow{775\ K} ReCl_5+ReCl_3$$

$$2R+3Br_2 \xrightarrow{775\ K} 2ReBr_3$$

Rhenium is slowly attacked by concentrated H_2SO_4 and the action is fast with conc. HNO_3.

$$2Re+14HNO_3 \rightarrow 2HReO_4+14NO_2+6H_2O$$

$$3Re + H_2SO_4 \rightarrow 2HReO_4+7SO_2+6H_2O$$

Rhenium combiues with sulphur to form the disulphide ReS_2. With phosphorus it forms a number of phosphides Re_2P, ReP, ReP_2, ReP_3, with arsenic it forms R_3As_7 while with sillicon the sillicide $ReSi_2$.

Rhenium readily forms alloys with Nb, Ta, Mo, W, Fe, Co, Ni and platinum metals. Rhenium with tungsten appears to form the componnd Re_3W_2.

When rhenium is fused with alkali metal, hydroxides in presence of oxygen, alkali metal perrhenates are obtained.

$$Re+4KOH+7O_2 \rightarrow 2HReO_4+2H_2O$$

Rhenium alloys are hard and have great mechanical strength which is retained even at high temperatures and alloys with Ni, Cr and Mo are resistant to heat and acids.

In a number of chemical reactions rhenium powder and its compounds are employed as catalytic agents.

Because of the shining look and excellent corrosion resistance, it is used in making jewellery.

Perrhenic acid and perrhenate are used for the gravimetric precipitation of potassium.

Rhenium is used in the filaments of incandescent lamps and thermionic emission tubes.

Rhodium [Greek *rhodon*, a rose, so called because of the colour of its salt solutions] **Rh.** A 4 d element of the 6th period of the Periodic Table of Elements, atomic number 45, atomic mass 102.905, a platinum family metal. One stable isotops, ^{103}Rh. Discovered in 1803 by Wollaston.

Properties A silvery bluish metal, harder and higher melting than platinum and palladium. Very inactive chemically, insoluble in acids. The main oxidation state in compound +3. Like platinum forms various complex ions.

Occurrence Accompanies platinum and platinum family metal.

Uses In the production of stable to tarnishing coating with a high reflective power. Alloys with platinum are used in the manufacture of chemical ware, in thermocouples, as catalysts, and in jewelry.

Rubidium [Latin *rubidus*, red, from the red lines in the spectrum] **Rb.** A Group IA element of the 5th period of the Periodic Table of Elements, atomic number 37, atomic mass 85.47, an alkali metal; exists as a mixture of two isotopes, ^{85}Rb (statble) and ^{87}Rb (radioactive). Discovered in 1861 by Bunsen and Kirchhoff in the spectrum of lepidolite (a mineral).

Properties A soft silvery white metal, very reactive, ignites in the air, reacts with water and acids with explosion. The oxidation state in compounds +1.

Occurrence Together with cesium in carnallite and lepidolite.

Uses In photocells, daylight lamps. Rubidium salts are used in the analytical chemistry and in medicine.

Ruby [Latin *rubeus* red]. A mineral, a transparent varietly of corundum, Al_2O_3. Colour from pale pink to deep red, a precious stone. Synthetic rubies are used in the manufacture of jewel bearings, e.g. in watchmaking. Single crystals of ruby are used as laser material.

Rust. Rust is a mixture of ferric hydroxide, $Fe(OH)_3$ and ferric oxide, Fe_2O_3 and is produced by the action of water on iron in presence of dissolved oxygen and sometimes also carbon dioxide. A number of theories have been put forward to explain the phenomenon of rusting out of which the electrochemical theory is more probable.

According to this, it is believed that chemically non-uniform surfaces of commercial forms of irom and steel behave like small electric cells (or corrosion couples) in presence of water containing dissolved oxygen and carbon dioxide. The layer of liquid water on the surface of the moist iron dissolves oxygen and carbon dioxide. In polluted atmosphere of industrial areas and on ships or near the sea some sulphur dioxide is also absorbed. Thus the metal is soon in contact with a solution of electrolyte and a chemical depolarizer.

In the initial stages of rusting, ferrous ions (Fe^{2+}) pass into solution at the anodic areas while hydrogen ions (H^+) originating from the water or suitable electrolytes (e.g. H_2CO_3) are discharged at the cathodic areas. The other ions (OH^- and HCO_3^-) migrate to the anodic area.

Dissolved oxygen oxidizes hydrogen to water at the cathode and thus acts as a depolarizer. It oxidizes ferrous ions to ferric ions at the anode. Hydroxyl ions present at the anode combine with Fe^{3+} ions there forming ferric hydroxide or hydrated ferric oxide—a deposit of rust.

Ruthenium [Latin *Ruthenia*, Russia: so called because first found in ores from the Urals] **Ru**. A 4 d element of the 5th period of the Periodic Table of Elements, atomic number 44, atomic mass 101.07, belongs to the platinum family, Discovered in 1844 by Klaus.

Properties A silvery white metal, resembles platinum, high-melting, very hard even at high temperatures. The most valuable properties are infusility, hardness, chemical stability, the ability to accelerate some chemical reactions. The most typical oxidation states are +3, +4, and +8. Readily forms complex compounds.

Occurrence Found together with other platinum family metals.

Uses As a catalyst, a hardener for platinum and paladium (in the manufacture of instruments with sharp tips), a component of electric contact alloys, in jewelry, etc.

Rutile, TiO_2. Natural titanium dioxide. Usually coloured (dark yellow, brown, red, or black). Used in the manufacture of ferro-titanium, white pigments, details with high dielectric constants. Synthetic rutile single crystals can be used as materials for rectifiers for high-temperature operating conditions, cut crystals to imitate diamond. Pure rutile crystals with certain admixtures are used in lasers.

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Saltpetre. KNO_3, saltpetre; $NaNO_3$, Chile saltpetre; NH_4NO_3, Norway saltpetre; $Ca(NO_3)_2$, lime salpetre. Used as nitrogen fertilizers.

Samarium (Discovered in the mineral samarskite named after Russian mine official Samarkii) **Sm**. A 4 f element of the 6th period of the Periodic Table of Elements, atomic number 62, atomic mass 150.35, belongs to lanthanides. Discovered in 1879 by Lecoq de Boisbaudran, isolated in 1901. *Properties* The oxidation states in compounds +2, +3. Compounds of Sm(II) are strong reducing agents.

Uses An alloying component, the manufacture of dyes, phosphors, and catalysts; somarium oxides are used as constituents of protective ceramic coatings in nuclear energy devices.

s-Block. The elements of Groups IA and IIA comprise the s-block elements. Group IA elements have the general configuration as ns^1 where n is the principal quantum number of the outermost shell These outer configurations are preceded by noble gas configurations.

Group IIA elements have the general electronic configuration ns^2 where n stands for the outermost shell. The s orbitals are stabilized with electrons in these atoms.

Scandium. It is the first element of 3d reries with electronic configuration, $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1\ 4s^2$. It occurs in nature only in the combined state. Its importent mineral is monazite sand. The concentration of the metal is low and it is difficult to get it in the pure state. It is, however, obtained by electrolysis of its fused chloride. The addition of a small amount of sodium chloride helps in lowering the melting point of $ScCl_3$.

Schodinger wave equation. An Austrian Scientist Erwin Schrodinger, in 1926, proposed that if electron is wave-like, it should obey the same equation as all other known types of wave motion obey. On the basis of this he substituted de Broglie relation $\left(\text{i.e. } \lambda=\frac{h}{mv}\right)$ into the classical equation for wave motion. The equation thus obtained should describe the wave nature of the electron and is called Schrodinger wave equation. This equation can be written in several forms. One of the simplest forms is

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\delta^2\psi}{\delta z^2}+\frac{8\pi^2 m}{h^2}\ (E-V)\psi=0$$

where E=total energy of electron i.e. kintic energy (K.E.)
+potential energy (P.E.)

V=Potential energy of the electron, i.e. work done against the attractive force when the electron moves away from the nucleus.

m=Mass of the electron

h=Planck's constant.

The Greek ψ (*psi*) is called "wave function". It is the mathematical function expressed in terms of the polar coordinates (r, θ and ϕ).

The symbol $\frac{\delta^2\psi}{\delta x^2}$ tells us what mathematical operations must be done upon ψ to solve for E. The symbol ψ refers to the amplitude of the wave and hence ψ^2 gives the probability of finding electron in any point in space.

Selenic acid H_2SeO_4. It is obtained by the oxidation of selenious acid as:

$$H_2SeO_3+Cl_2+H_2O \longrightarrow H_2SeO_4+2HCl$$
$$H_2SeO_3+PbO_2 \longrightarrow H_2SeO_4+PbO$$

It is a colourless crystalline solid (m.p. 331 K). It is soluble in water and the reaction is exothermic. It decomposes on heating.

$$2H_2SeO_4 \longrightarrow 2SeO_2+2H_2O+O_2$$

It is a strong oxidizing agent.

Selenious acid, H_2SeO_3. It is obtained by action of nitric acid on selenium or by dissolving selenium dioxide in water.

$$Se+HNO_3 \longrightarrow H_2SeO_3+H_2O_2+4NO_2$$
$$SeO_2+H_2O \longrightarrow H_2SeO_3$$

Selenious acid is colourless crystalline solid, hygroscopic in nature. It is readily soluble in water. It is easily reduced by sulphur dioxide to selenium and oxidized by strong oxidizing agents like chlorine. bromine, etc. to selenic acid.

$$H_2SeO_3+2SO_2+H_2O \longrightarrow Se+2H_2SO_4$$
$$H_2SeO_3+Cl_2+H_2O \longrightarrow H_2SeO_4+2HCl$$

Selenium [Greek *selene*, the moon, so called by association with tellurium whose name derives from Latin *tellus*, the earth] Se. A Group VIA element of the 4th period of the Periodic Table of Elements, atomic number 34, atomic mass 78.96. Discovered in 1817 by Berzelius.

Properties Like sulphur has several allotropic forms such as amorphous selenium and crystalline selenium. The latter is a brittle solid with a grey colour and metallic lustre. The grey form has an interesting property of increasing its electric conductivity substantially when subjected to the action of light; this property is utilized in selenium photocells. The oxidation states in compounds −2, +4, +6. Stable to the action of oxygen, water. and dilute acids at room temperature. Dissolves in alkalis, concentrated nitric acid, and aqua regia. At elevated temperatures, combines readily with quite a number of elements. Hydrogen selenide, H_2Se, is a colourless poisonous gas with a disagreeable odour, a weak acid in aqueous solutions. Salts of hydroselenic acid, selenides, resemble sulphides. Burning of selenium in the air gives SeO_2 a solid substance; unlike SO_2 it mostly behaves as an oxidizing agent and readily undergoes reduction to free selenium. Strong oxidants can convert SeO_2 to selenic acid, H_3SeO_4, a crystalline solid.

Occurrence Not abundant, occurs as an admixture to native sulphides (FeS_2, PbS, etc.).

Manufacture From the flue dust obtained in burning pyrites in the manufacture of sulphuric acid.

Uses In the manufacture of rectifiers and photocells, in the synthesis of selenides having semiconductor properties and used in thermocells, photoresistors, as phosphors.

Selenium dioxide, SeO_2. It is obtained, when selenium burns in air or oxygen or treated with nitric acid.

$$Se + O_2 \longrightarrow SeO_2$$
$$Se + 4HNO_3 \longrightarrow H_3SeO_3 + 4NO_2 + H_2O$$
$$H_2SeO_3 \longrightarrow SeO_2 + H_2O$$

It is a white crystalline solid which sublimes on heating. It is soluble in water and gives selenious acid hence it is also known as anhydride of selenious acid.

It is used in oxidation of aldehydes and ketones.

Selenium trioxide, SeO_3. It is obtained by the reaction of ozone on selenium dissolved in selenium oxychloride.

$$Se + O_3 \longrightarrow SeO_3$$

It is a pale yellow solid. It is soluble in water and forms selenic acid.

$$SeO_3 + H_2O \longrightarrow H_2SeO_4$$

It decomposes at 393K as

$$2SeO_3 \longrightarrow 2SeO_2 + O_2$$

Semiconductor. A semiconductor is a material whose electrical conductivity increases with temperature. Heat frees electrons from specific sites in the semiconductor lattice and thereby increases the number of conduction electrons. This effect more than cancels the effect of the increased lattice vibrations. The conductivity of a semiconductor is usually less than that of a good conductor and more than that of a good insulator; it is, in addition, unsually sensitive to the presence of impurities and lattice defects.

Semimetal. There is no sharp distinction, either chemical or physical, between a metal and a nonmetal. The elements "straddling the fence" are sometimes classified as semimetals.

Sequestering agent. A sequestering agent is a chelating agent, i.e. a multidentate ligand. One of the functions of the builder in a detergent formulation is to sequester, or complex, ions like Mg^{2+} and Ca^{2+} so that they cannot interfere with the action of the surfactant.

Shielding or screening effect. Actual nuclear charge is shielded from the outer electrons by electrons that occupy shells between the outer electron and the nucleus. As a result, the valence electron does not experience the full magnitude of the actual nuclear charge. The shielding thus provided is known as shielding effect or screening effect. In other words, the inner orbitals act as a shield or screen between the nucleus and the valence electron.

The screening effect is denoted S by and is estimated by some empirical rule. For a particular electron configuration it is obtained as a constant value.

Silicate. A salt of a silicic acid, made by fusing SiO_2 together with an alkali or a metal carbonate:

$$SiO_2+2NaOH \rightarrow Na_2SiO_3+H_2O$$
$$SiO_2+Na_2CO_3 \rightarrow N_2SiO_3+CO_2$$
$$SiO_2+4NaOH \rightarrow Na_4SiO_4+2H_2O$$
$$SiO_2+Cao \rightarrow CaSiO_3$$

Very abundant in nature, earth's crust mainly consists of silica, SiO_2, and various metal silicates. Examples of native silicates are feldspars, mica, clays, asbestos, and talc. They occur as constituents of a number of rocks such as granite gneiss, basalt, various varieties of shale. Many precious stones, e.g. emerald, topaz, aquamarine, are natural crystals of various silicates.

Silicic acids (hydrated silica). Very weak, slightly soluble in water substances. Salts of metasilicic, H_2SiO_3 ($SiO_2 \cdot H_2O$), orthosilicic, H_4SiO_4 ($SiO_2 \cdot 2H_2O$), and some other silicic acids, $SiO_2 . nH_2O$, are known. Silica hydrates containing more than two water molecules per one SiO_2 unit can hardly exist as individual substances, but quite a number of their salts have been isolated. Silicic acids give colloidal aqueous solutions. Metal silicates are used in the manufacture of paper, in the textile industry, for treatment of water, as binding materials; they are very abundant in nature.

Silicide. A compound of silicon and a metal. Silicides are formed at high temperatures. They are made either by the synthesis from the elements or by the reduction of a metal oxide with silicon:

$$MO+2Si \rightarrow MSi+SiO_2$$

Vanadium silicide, V_3Si is used as superconductor and rhenium silicide, ReSi, as a semiconductor. Many silicides are constituents of refractory materials (e.g. $MoSi_2$). Ferrosilicon has important practical applications.

Silicon [Latin *silex*, *silicis*, flint] Si. A Group IVA element of the 3rd period of the Periodic Table of Elements, atomic number 14, atomic mass 28.086, discovered in 1823 by Berzelius.

Properties A dark-grey crystalline substance, the oxidation states in compounds +2 and, more often, +4, reacts with many ubstances at elevated temperatures, at 675 K reacts with oxygen to give SiO_2. Reduces many oxides upon heating. Dissolves in a mixture of hydrofluoric and nitric acids, rapidly dissolves in alkalis with release of hydrogen reacts with many molten metals to form metal silicides; does not combine with hydrogen.

Occurrence Next to oxygen, the most abundant element; occurs as SiO_2 and metal silicates.

Manufacture Very pure Si is obtained by the reduction of $SiCl_4$ with zinc, hydrogen, or by thermal decomposition of SiJ_4 or SiH_4. Silicon is manufactured by reducing silica with coke.

Uses In metallurgy as a deoxidizer, contained in many iron, copper, aluminium, and other alloys. Also employed for the synthesis of organosilicon compounds and various other materials, in the manufacture of semiconductors, photocells, rectifiers, transistors, etc. Silicon and various silicates (clays, feldspar, mica, etc.) are used in large ammount in the manufacture of glass, cement, in the electric engineering, and other fields of industry.

Silicon carbide, SiC. One of the most important carbides used as an abrasive, etc.

Silicone. A group name for high molecular mass organosilicon compounds containing oxygen. Silicone rubber is a good electrical insulator, resistant to heat and to frost; remains elastic in the range 215-675 K. It is widely applied in the manufacture of thermally resistant spacers, memberanes, valves, details for projector units, electrical insulators, etc. Numerous organosilicon polymers are employed as lubricants stable to heating and freezing and fluids operating at temperatures of 175 K to 525 K, and render various materials hydrophobic (e.g. fabrics, paper, glass ceramics, building materials). The are also used in the manufacture of lacquers and dyes.

Silicon monoxide, SiO. A vitreous amorphous substance, stable to the action of oxygen under normal conditions.

Silumin. An alloy of aluminium and silicon containing up to 14 per cent silicon. As strong as steel being far lighter than that material, very good for casting. Used in mechanical engineering.

Silver. Silver is a relatively active metal. It is found in nature in the form of compounds. The main ore from which silver is produced is argentite. Silver is recovered from this ore by cyanide extraction, zinc reduction or electrolytic process.

Silver is found in water, soil and ambient air. Sea water has been reported to contain silver concentrations of 0.055-1.5 μg/L. Much higher concentrations (0.03 mg/L) have been reported in waste water. Molluses collected from coastal areas of the North sea have been reported to contain silver concentrations of up to 2.0 mg/kg. Drinking water, not treated with silver for disinfection purposes, usually contains extremely low concentrations of silver. A range of non-detectable to 5 μg/L was reported for finished waters. Treated water may contain 50 μg/L or even slightly higher concentration. Silver is infrequently found in rivers of the united states in concentration of only about 1 μg/L. Concentrations of 5-150 μg/L have been reported in sewage sludge.

Soil concentrations of silver vary greatly by geological area. Granite igneous rock in Nevada has been reported to contain upto 50 mg/kg silver. Coal fly-ash has been reported to contain upto 15 mg/kg silver.

Silver has been measured in air as a result of anthropogenic activity. Air concentrations of silver have been reported to be about 2ng/m^3. The emission of silver iodide crystals during cloud seeding has been estimated to result in a silver concentration in air of about 0.1 ng/m^3. Silver concentrations in rain water as a result of this process were estimated to be between 0.04 pg/mL and 5 ng/mL.

Concentration of silver in cigarettes are low. Because of its high boiling point, most of the silver in cigarettes is probably not inhaled.

The concentration of silver in kidneys, liver and spleen of normal people has been reported to be about 0.4, 0.7 and 2.7 mg/kg respectively, on a dry weight basis. Normal concentration in skin was reported as 0.035±0.015 mg/kg dry weight. The concentration of silver in urine varies between 0.006 and 0.015 mg/day and between 0.02 and 0.11 mg/kg in feces has been reported.

Silver is commonly used in the coins, jewellery and tableware. This element is also utilized as a component of various alloys and solders with copper, cadmium and lead. It is extensively used in photographic processing, in the manufacture of electrical apparatus and mirrors, in dentistry, and in the treatment of burns. Silver salts, because of their germicidal properties are also used as drinking water disinfectants and as prophylactic agents against gonorrheal infection in the newborn. Silver has also anticancer properties according to Aryoveda. Silver is also used as a catalyst, e.g. the production of formaldehyde from methanol and air by means of silver screens. It is also used in batteries, as antiseptic to destroy the bacteria in water and in aircraft engine bearings.

There are spectrographic, colorimetric and polarographic techniques for measurement of silver. The detection limit for spectrographic and dithizone colorimetric methods has been put at 0.01 mg/L for a 20 mL sample. The detection limit for polarographic techniques is 5×10^{-6}M Ag. Atomic absorption (detection limit 2 μg/L) and neutron activation (detection limit 2 ng) may also be used and are relatively accurate. A reference listing of detection limits and other comments on the analysis for silver are reported.

Though AAS and neutron activation methods are very convenient from the analyst's point of view, the accessibility of the instrumental facility to a common analyst/chemist becomes a hurdle in the choice and one looks for some alternate instrument or method. Spectrophotometric methods then become the methods of choice. Spectrophotometric procedure is popular, commonly employing dithizone to develop orange-yellow dithizonate.

Among the indirect methods suggested for silver determination are diethyldithiocarbamate of copper [$Cu(DDTC)_2$], mercupral, 1,10-phenanthroline, halogenated derivatives of fluorescein, and sulpharsazen. In these methods silver displaces the metal ion and decolorises the reagent. Other organosulphur reagents used for the direct determination of silver include dithiol, thiomichler's ketone, diallyldithiocarbamidohydrazine (Dalzin), and 2-amino-6-methylthio-4-pyrimidine carboxylic acid.

Markham has determined silver by extracting into benzene the ion-pair formed between $Ag(CN)_2^-$ and the basic dye, crystal violet. Colorimetric reagents including 2,3-naphthotriazole, Nile Blue A, and phenylenediamine have been used to determine silver. Largeı amounts of silver can be determined turbidimetrically after reduction to yield a silver solution, as the silver sulphide solution or as the silver chloride solution.

Among all the spectrophotometric methods for determining silver, the following two are particularly important; the extractive dithizone method and the non-extractive rhodamine method. Both are of similar selectivity, but the dithizone method is more sensitive and more accurate.

Silver halides. All the four silver halides, i.e. AgF, AgCl, AgBr and AgI, are known. Except the fluoride, others are quite insoluble. Silver bromide is soluble in concentrated thiosulphate soluble due to complex formation:

$$AgBr + 2S_2O_3^{2-} \longrightarrow [Ag(S_2O_3)_2]^{3-} + Br^-$$

This reaction in used in fixing the image on the photographic film since the thiosulphate dissolves away the unaffecetd silver bromide from the exposed film. Silver halides (except silver iodide) are light sensitive and these are used in making photographic films.

Silver nitrate, $AgNO_3$ (Lunar caustic). It is prepared by dissolving silver metal in warm dilute nitric acid.

$$3Ag + 4HNO_3 \longrightarrow 3AgNO_3 + 2H_2O + NO$$

Silver nitrate is an important laboratory reagent and is used for detection of many anions like halides, $S_2O_3^{2-}$, S^{2-}, CrO_4^{2-} and PO_4^{3-}.

$Ag^+ + Cl^- \longrightarrow AgCl$
(white precipitate soluble in ammonium hydroxide)

$Ag^+ + Br^- \longrightarrow AgBr$
(pale yellow ppt. slightly soluble in NH_4OH)

$Ag^+ + I^- \longrightarrow AgI$
(yellow ppt. insoluble in ammonium hydroxide)

$2Ag^+ + S_2O_3^{2-} \longrightarrow Ag_2S_2O_3$
(white ppt, turning yellow, brown and black)

$2Ag^+ + S^{2-} \longrightarrow Ag_2S$
(black precipitate)

$2Ag^+ + CrO_4^{2-} \longrightarrow Ag_2CrO_4$
(brick red precipitate)

$3Ag^+ + PO_4^{3-} \longrightarrow Ag_3PO_4$
(yellow precipitate soluble in ammonium hydroxide)

It is also used for volumetric and gravimetric determinations of halide ions. In industry, the salt finds many applications. It is used in silvering of mirrors and silver plating, preparing inks for clothes, hair dyes and medicines.

Sodium. Two of the widely used compounds of sodium, i.e. sodium chloride (common salt) and sodium carbonate (washing soda) have been known since very early times. Since its salts are highly stable, the isolation of the metal could not be achieved till 1807 when Davy obtained metallic sodium by the electrolysis of fused caustic soda.

Sodium occurs only in the combined state:

Sodium chloride, common salt found as rock salt, in sea water and in some inland lakes.

Sodium nitrate as Chile saltpetre or caliche in Chile (South America).

Sodium carbonate found as an efflorescent substance in the arid regions or many hot countries.

Borax, $Na_2B_4O_7.10H_2O$ is available in the crude form called tincal in California, Tibet and India (Ladakh and Kashmir).

Sodium is extracted on a commercial scale by the electrolysis of fused caustic soda (Castner's Process) or fused sodium chloride (Downs' Process).

Uses For the preparation of sodium peroxide, sodamide and sodium cyanide, tetraethyl lead, etc.

Sodium amalgam is employed as a reducing agent.

As a reagent in organic chemistry.

As a deoxidizing agent in the preparation of light alloys and some rare earth metals from their oxides.

It acts as a catalyst in the polymerization of isoprene (C_5H_8) into raw rubber (artificial rubber).

Sodium bicarbonate. It is the primary product obtained during the Solvay process. It can also be produced by passing carbon dioxide through a cold and concentrated solution of sodium carbonate.

$$Na_2CO_3+CO_2+H_2O \longrightarrow 2NaHCO_3$$

Sodium bicarbonate is less basic than sodium carbonate and is used as a medicine to cure acidity in the stomach. It is also used in effervescent drinks and as a constitutent in baking powders.

Sodium carbonate. The industrially important compound sodium carbonate, $Na_2CO_3.10H_2O$ is manufactured by ammonia-soda (also called Solvay) process.

Sodium carbonate, commonly called washing soda, is used for washing and also as a reagent in the laboratary. Industrially, it is used in the manufacture of soap and glass, in the treatment of hard water, in paper-making and in the preparation of many other sodium salts.

Sodium hydroxide. This is usually manufactured by the electrolysis of a saturated solution of sodium chloride using mecury cathode and graphite anode in the Castner-Kellner cell.

Both sodium hydroxide and potassium hydroxide are used in the manufacture of soap. Sodium hydroxlde is an important laboratory reagent; it is used for absorbing carbon dioxide and other gases.

Sodium hypochlorite, $NaOCl$. It is prepared by the action of chlorine with cold dilute solution of sodium hydroxide.

$$2NaOH+Cl_2 \longrightarrow NaOCl+H_2O+NaCl$$

On large scale, it is prepared by the electrolysis of brine in an undivided cell. The chlorine liberated at the anode reacts with sodium hydroxide to form sodium hypochlorite.

Its solution cannot be concentrated by heating because it decomposes as:

$$3NaOCl \longrightarrow 2NaCl+NaClO_3$$

On keeping, it loses oxygen.

$$NaOCl \longrightarrow NaCl+(O)$$

It reacts with dilute acids to form hypochlorous acid, hence it acts as a strong oxidizing and bleaching agent.

$$NaOCl+HCl \longrightarrow HOCl+NaCl$$
$$HOCl \longrightarrow HCl+(O)$$
$$2HCl+(O) \longrightarrow H_2O+Cl_2$$
$$Na_3AsO_3+(O) \longrightarrow Na_3AsO_4$$
$$2I^-+(O)+2H^+ \longrightarrow I_2+H_2O$$
$$2Pb(CH_3COO)_2+4NaOCl \longrightarrow 4CH_3COONa+PbCl_2+PbO_2$$

Sodium peroxide, Na_2O_2. It is prepared by heating sodium in excess of air free from carbon dioxide. Sodium is cut into thin slices and placed in aluminium trays. With the help of a moving belt the trays are slowly moved through a heated tube (675 K) in a current of air, free from moisture and carbon dioxide blown from the opposite direction. By the time the tray moves out of the tube, the whole of the sodium gets converted into sodium peroxide.

It is used as an oxidizing and bleaching agent.

Sodium phosphate, tribasic (trisodium orthophosphate) **$Na_3PO_4.12H_2O$**. Used for softening water and to remove oil from metal and cloth, for washing glass and floor.

Sodium salts. Sodium forms salts with all acids. Sodium arsenate, Na_3AsO_4 and arsenite, $NaAsO_2$ (Na_3AsO_3) are pesticides; sodium bromide, NaBr is used in medicine and photography; sodium dichromate, $Na_2Cr_2O_7$ is an oxidizing agent, used for tanning leather; sodium carbonate, Na_2CO_3 and bicarbonate, $NaHCO_3$ are given in separate entries; sodium nitrate (Chile saltpetre), $NaNO_3$ is a nitrogen fertilizer; sodium nitrite, $NaNO_2$ is employed in the synthesis of azo dyes and in medicine; sodium silicate, Na_2SiO_3 is also called soluble or liquid glass (see a separate entry); sodium sulphate, Na_2SO_4, is used in the manufacture of glass, paper, cellulose, leather, soap, and in the textile industry; sodium sulphide, Na_2S in the manufacture of sulphide dyes, in the textile and leather industries, in flotation processes, in the analytical chemistry for separating element mixtures; sodium hydrosulphide, NaHS is used in the manufacture of synthetic silk and leather; sodium polysulphides, Na_2S_n in the floatation processes and agriculture; sodium sulphite, Na_2SO_3 in photography, medicine, and in the manufacture of synthetic fibre; sodium hydrosulphite, $NaHSO_3$ is a preservative, its other uses are bleaching and dyeing of fabrics; sodium thiosulphate, $Na_2S_2O_3$ is used in photography, medicine, and in the analytical chemistry; sodium fluoride, NaF is a preservative for wood, is used in agriculture, in the manufacture of enamels, and as a flux; sodium phosphates have washing action, soften water, are employed in concentrating ores, in the food industry, etc.; sodium chloride (table salt) is a starting material for the production of soda, sodium hydroxide, chlorine, and sodium sulphate, it is also used in medicine, agriculture, and for seasoning and preserving food.

Sodium silicate (soluble glass, liquid glass, water glass). A vitreous substance, made by fusing together SiO_2 and soda. Aqueous solutions are used in the manufacture of cement resistant to the action of acids, for impregnating fabrics, in preparation of fire-proof paints for wood, for hardening mellow ground, etc.

Spin quantum number. This quantum number is designated as m_s. This is due to the spinning of electron along its own axis. As the spinning can be in two possible directions (i.e. clockwise and anticlockwise), *ms* can have two values, $+\frac{1}{2}$ and $-\frac{1}{2}$ in terms of its spin angular momenta. These are often represented by putting arrows in the opposite directions ↑ and ↓. Thus in each orientation as per the megnetic quantum number, the number of electron is two.

Spongy platinum. It is a soft and spongy form of platinum, grey in colour and finds use as a catalyst in a number of chemical processes. It causes a mixture of hydrogen and oxygen to unite with explosion. Coal gas can be ignited by spongy platinum and is, therefore, used in "selflighting" Bunsen burners.

It is prepared by the ignition of ammonium chloroplatinate.

$$(NH_4)_2PtCl_6 \rightarrow Pt + 2NH_3 + 2HCl + 2Cl_2$$

Standard deviation. Precision is usually expressed as standard deviation, σ. Mathematically,

$$\sigma = \left(\frac{\Sigma(x_i - \mu)}{N}\right)^{\frac{1}{2}}$$

(where x_i = individual measured value

μ = mean of the number of measurements

N = number of values measured).

Steel. It is an alloy of iron and carbon containing admixtures of manganese, silicon, sulphur, and phosphorus. The most familiar carbon steel contains 0.05 to 1.5% C, 0.1 to 1% Mn, up to 0.4% Si, up to 0.08% S, and up to 0.18% P. Alloyed steel contains larger admixtures or admixtures of other elements. The elements used to alloy steel are Cr, Ni, Mn, Cu, W, Mo, V, Co, Ti, Nb, Al, Zr, and Ta. Alloyed steels have good mechanical and physicochemical properties. They are used in the manufacture of details of mechanisms, instruments, cutting tools, stamps, etc. Stainless steels containing up to 12% Cr are resistant to corrosion in the air, in acids, alkalis, and solutions of salts. The addition of chromium, silicon, and aluminium makes steel heat-resistant, and the saturation of its surface by nitrogen (nitriding) strongly increases its wearability. Steel is usually made from pig iron by oxidizing some part of carbon contained there. This technique is applied most widely in the present day metallurgy. The other method is the reduction of iron in iron ores and the introduction of required amounts of carbon and other admixtures.

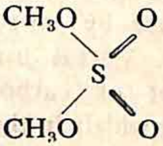
Strength of a solution. The amount of a substance dissolved in one litre of a solution when expressed in grams is termed as the strength of the solution. For example, if 8.0 g of a substance is dissolved in 1000 mL, its strength is 8.0 g/L.

Strontium [from Strontian, town in Scotland where the mineral containing strontium was found] Sr. A Group IIA element of the 5th period of the Periodic Table of Elements, atomic number 38, atomic mass 87.62. Discovered in 1790 by Crawford. The ^{90}Sr ($t_{1/2}=28$ years) radioactive isotope has found practical applications. This long-lived isotope is formed in fission of uranium (nuclear tests), dangerous to man.

Properties A silvery metal, in its chemical properties resembles other alkaline earth metals (Ca, Ba). Turns flames red, the property is utilized in pyrotechnics. The oxidation state in compounds +2.

Occurrence The chief ores are strontianite, $SrCO_3$, and celestite, $SrSO_4$.

Sulphate. A salt of sulphuric acid, H_2SO_4. Neutral sulphates are crystalline substances, mostly soluble in water (except $BaSO_4$, $PbSO_4$, etc.). Often cystallize in the form of hydrates, e.g. various vitriols (blue vitriol or copper sulphate, $CuSO_4 \cdot 5H_2O$; green (iron) vitriol or ferrous sulphate, $FeSO_4 \cdot 7H_2O$; white (zinc) vitriol, $ZnSO_4 \cdot 7H_2O$). Ammonium sulphate is used as a fertilizer, sodium sulphate in soap, paper, glass manufacture, copper sulphate in agriculture, etc. Metal hydrosulphates containing the HSO_4^- anion are used to convert substances insoluble in acids (e.g. calcined oxides of aluminium, chlromium, iron) into soluble forms by fusing. Organic sulphates are esters of sulphuric acid, e.g. dimethyl sulphate:



Sulphide. A compound of a metal and sulphur; the term is also applied to certain binary compounds of sulphur and nonmetals, e.g. B, Si, P, and As. Sulphides are formed in various reactions:

$$Fe + S \rightarrow FeS$$
$$2CdO + 3S \rightarrow 2CdS + SO_2$$
$$TiO_2 + CS_2 \rightarrow TiS_2 + CO_2$$

Sulphur [Latin *sulphur*, brimstone] S. A Group VIA element of the 3rd period of the Periodic Table of Elements, atomic number 16, atomic mass 32.064, known to the ancients.

Properties A yellow solid, insoluble in water, soluble in carbon disulphide and benzene. Several allotropic forms of sulphur are known (rhombic, monoclinic, etc.). The oxidation states in compound −2, +4, +6, +2 (rare).

Occurrence Found native and in compounds, e.g. pyrite, FeS_2.

Extraction Native sulphur is molten underground and raised to the surface by superheated water under pressure.

Uses Far the larger proportion of sulphur is used in the manufacture of sulphuric acid. Other uses are pulp and paper, carbon disulphide, dyes, matches, gunpowder, rubber vulcanization, medicine, agriculture fungicide. Purified sulphur with some organic admixtures (petroleum jelly, persic oil, etc.) is used to combat various skin diseases and as an antiseptic; these mixtures are also employed to destroy plant pests (spraying and dusting of plants), in cosmetics.

Sulphuric acid (Oil of vitriol, battery acid) **H_2SO_4.**

Properties A colourless oily liquid, density 18.4 (96 per cent H_2SO_4). Absorbs moisture with avidity, dissolves in water with release of much heat because of the formation of the hydrates, $H_2SO_4.H_2O$, $H_2SO_4.2H_2O$, and $H_2SO_4.4H_2O$. Dissolves large amounts of SO_3 to give fuming sulphuric acid. Because of low volatility (b.p. 603 K) displaces more volatile acids from their salts. At elevated temperatures releases SO_3 which combines with moisture to produce fog of H_2SO_4. Sulphuric acid is an effective dehydrating agent commonly used to dry gases; it causes charring of carbohydrates because of the abstraction of water.

$$C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12C + 11H_2O$$

At elevated temperatures concentrated H_2SO_4 is a strong oxidizing agent. Sulphuric acid is a strong dibasic acid, undergoes stepwise dissociation in aqueous solutions.

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \rightleftharpoons 2H^+ + SO_4^{2-}$$

Sulphurous acid. This is one of the important compounds in which sulphur is in +4 oxidation state. It in produced when SO_2 dissolves in water. This acid is not very stable and pure H_2SO_3 cannot be isolated. Sulphurous acid is a weak, diprotic acid and forms two series of salts; normal salts (e.g. Na_2SO_3, sodium sulphite) and acid salts (e.g. $NaHSO_3$, sodium bisulphite). These salts are often prepared by bubbling SO_2 through a solution of hydroxide.

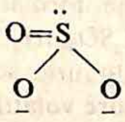
$$2OH^- + SO_2 \longrightarrow SO_3^{2-} + H_2O$$

On further passing the gas, acid salt is formed.

$$H_2O + SO_3^{2-}(aq) + SO_2 \longrightarrow 2HSO_3^-$$

Both the series of salts can be isolated. Since H_2SO_3 is unstable, addition of any non-oxidizing acid to a sulphate, liberates SO_2. This is a common method of preparation of SO_2.

H_2SO_3 and SO_2 are compounds of sulphur in oxidation state +4. Hence these compounds can act both as reducing as well as oxidizing agents. However, sulphites are commonly used as reducing agents. The tetrahedral structure of sulphite ion is given below:

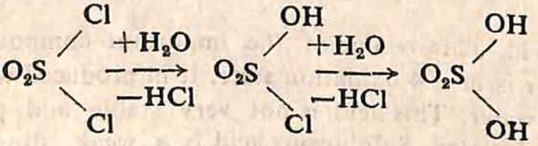


Sulphuryl chloride, SO_2Cl_2. It is obtained by the direct combination of sulphur dioxide and liquid chlorine in the presence of camphor (catalyst) or by heating chlorosulphonic acid in the presence of mercuric sulphate catalyst.

$$SO_2 + Cl_2 \xrightarrow{\text{camphor}} SO_2Cl_2$$

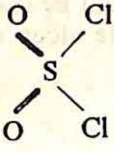
$$2HO.SO_2.Cl \xrightarrow{HgSO_4} SO_2Cl_2 + H_2SO_4$$

It is a colourless liquid with pungent smell (b.p. 342 K, sp. gr. 1.67). It hydrolyses with water as:



It is used a strong chlorinating agent for introducing sulphonic acid group or sulphonyl chloride group.

Its structure is tetrahedral as shown below:



Superoxide. A compound with oxygen in the $-^1/_2$ oxidation state is called a superoxide.

Superphosphate of lime. It is a mixture of calcium dihydrogen phosphate and calcium sulphate.

It is being manufactured by treating calcium phosphate (phosphorite rock or bone ash) with a calculated quantity of sulphuric acid.

$$Ca_3(PO_4)_2+2H_2SO_4+5H_2O\rightarrow Ca(H_2PO_4)_2.H_2O + 2CaSO_4.2H_2O$$

A large quantity of heat is produced which dries the products and a dry mixture of primary calcium phosphate and gypsum is obtained. This mixture is sold in market under the trade name 'Superphosphate of Lime'.

It contains 16 per cent of the available phosphorus as P_2O_5. It is an important fertilizer.

The most common phosphatic fertilizer used in India is single superphosphate containing 16 per cent phosphorus pentoxide, as it is suitable for soils of all kinds. Its response is maximum in netural soils, as phosphorus fixation occurs in acidic as well as in calcareous and alkaline soils In acidic soils it should be added with organic manures. The response of superphosphate is more on medium and heavy soils than on lighter soils because of low level of other nutrients. Since it contains water solucle phosphate, it comes in contact with soil immediately after application and may be converted into unavailable forms like tricalcium phosphate, ferric phosphate, aluminium phosphate, etc. depending upon soil reaction, the former in alkaline and calcareous soils and the latter two in acid soils. Therefore, superphosphate is usually added before sowing or very close to root zone (10 to 15 cm depth). It can be applied before sowing or along with planting. It is grey ash like powder with good storage quality. It should be stored in moisture proof godowns so that monophosphate does not get converted into di-or tri-phosphate.

T

Tantalum. [Greek *Tantalos*, mythological character] Ta. A 5 d element of the 6th period of the Periodic Table of Elements, atomic number 73, atomic mass 180.948. Discovered in 1802 by Ekeberg.

Properties A grey metal with a bluish cast, m.p. 3123 K hard but not brittle, workable. Very stable to the action of acids and other aggressive substances being superior to platinum in that respect. Reacts with fluorine at room temperature, only at elevated temperatures with other substances such as sulphur or halogens. The principal oxidation state +5.

Occurrence Does not occur native, found as admixtures to certain minerals (columbite, tantalite, etc.).

Uses In surgery to fasten broken bones (tantalum does not irritate living tissue and causes no harm to organisms), in various heat-resistant, hard, and high-melting alloys (rocket engineering, supersonics). In the manufacture of chemical instruments, laboratory ware, and crucibles.

Technetium. It is a transition metal produced artificially by bombarding molybedenum with neutrons and also during the fission of uranium. It is radioactive.

Symbol Tc; m.p. 2403 K b.p. 4893 K;

Tellurium. Tellurium was discovered in 1782 by Muller von Reichenstein, and named by Klaproth in 1798 from the Latin *tellus*, the earth. The element and its compounds were later on studied by Berzelius, who placed it in Group VIA along with sulphur and selenium.

It forms $2 \times 10^{-7}\%$ of the lithosphere and occurs in sulphide ores, particularly those of copper, and as the tellurides of gold and silver. The mineral tetradymite contains tellurium as the bismuth telluride, Bi_2Te_3. Some other minerals are:

Petzite $(Ag, Au)_2Te$; Hessite Ag_2Te

Sslvanite $(Au, Ag)Te_2$

Its principal source is the anode mud from electrolytic refining of copper which also is source of selenium.

From tetradymite The mineral is fused with sodium carbonate and the solid mass extracted with water. Air is passed through the aqueous solution when tellurium is precipitated.

$$Bi_2Te_3 + 3Na_2CO_3 \rightarrow Bi_2O_3 + 3Na_2Te + 3CO_2$$
$$2Na_2Te + O_2 + 2H_2O \rightarrow 4NaOH + 2Te$$

From anode mud The anode mud obtained during the electrolytic refining of copper is mixed with sodium nitrate (an oxidizing agent) and sodium hydroxide and fused. The aqueous extract containing sodium selenite and sodium tellurite is acidified when TeO_2 is precipitated. Sulphur dioxide is passed through the filtrate to get selenium. Tellurium dioxide is reduced by heating it with charcoal.

$$Te + 2NaOH + O_2 \rightarrow Na_2TeO_3 + H_2 + H_2O$$
$$Na_2TeO_3 + H_4SO_4 \rightarrow Na_2SO_4 + TeO_2 + H_2O$$
$$TeO_2 + 2C \rightarrow Te + 2CO$$

Alternatively, TeO_2 is dissolved in concentrated hydrochloric acid. On passing sulphur dioxide through this solution tellurium is precipitated.

The anode sludge may also be dissolved in fuming sulphuric acid. On diluting the solution and adding zinc dust tellurium gets precipitated.

Tellurium is added to lead to improve its resistance to heat, mechanical shock and corrosion. The addition of 0.5 to 1 percent of tellurium increases the machining qualities of copper to a very large extent. It has also been used for the electroplating of silver for producing a dark finish. Because of its high electrical resistance (highest amongst metals) it is used as a high resistance material.

Tellurium crystals are used in the detectors for wireless telephones. A solution of tellurium in sodium sulphide is used in photography as a toning agent. Tellurium is also used in colouring porcelain and glass; brown, blue or red colours are produced under different conditions.

Diethyl telluride is added in small amount to gasoline which can be used in high compression motors. This process, known as tellurization, doubles the mileage obtained from gasoline.

Tempering. It is the process of heating the hardened steel to a temperature much below redness and cooling it slowly. The product obtained is neither so hard nor so brittle.

Terbium. It is a soft ductile malleable silvery element of the lanthanide series of metals. It occurs in association with other lanthanides. One of its few uses is as a dopant in solid-state devices.

Symbol Tb; m.p. 1629 K; b.p. 3396 K.

Thallium [Greek *thallos*, a young, green shoot: from the green line in its spectrum which led to its discovery] **Tl.** A Group IIIA element of the 6th period of the Periodic Table of Elements, atomic number 81, atomic mass 204.37. Discovered in 1861 by Crookes by the spectral method. Natural thallium contains two isotopes, ^{203}Tl and ^{205}Tl.

Properties A bluish-white lead-like metal, tarnishes in the air. Does not react with water, but readily dissolves in acids. The oxidation states in compounds +1, +3,. Thallium hydroxide (thallous hydroxide), $TlOH$ is a strong base, whereas thallic hydroxide, $Tl(OH)_3$ shows only weak basic properties. Most univalent thallium salts are readily soluble in water except for thallous halides, $TlCl$, $TlBr$, and TlI which like the corresponding silver salts are almost insoluble and sensitive to the light.

Occurrence A scattered element, occurs as traces in various rocks.

Manufacture From sulphide ores of nonferrous metals; the chief source is flue dust from zinc smelting.

Uses Thallium compounds are used in photography, medicine, in the manufacture of optical glasses with high refractive indices. Thallous sulphide is used in high-sensitivity photocells, thallous sulphate as a rodent poison. Thallium metal is a component of some alloys for bearings and alloys resistant to acids.

Thomas meal. It is another important posphate fertilizer which is prepared by grinding the basic slag obtained as a by product in the manufacture of steel. It is a double salt of calcium phosphate and calcium silicate [$Ca_3(PO_4)_2.CaSiO_3$]. In the soil it decomposes slowly and supplies necessary phosphoric acid to the soil for a long period.

Thorium. Thorium is the first member of 5f-innertransition metal series or actinides. It has very similar properties with the other elements of actinides.

Thorium in the form of its oxide was discovered in a Norwegian mineral thorite ($ThSiO_4$) by Berzelius in 1828. He could isolate a very impure sample of the element by the reduction of the double fluoride of the elements with Na or K. Madam Curie and Schmidt (1898) discovered its radioactive nature. Lelyand and Hamburger prepared 98% pure thorium by distilling NaCl and $ThCl_4$ in evacuated cylinder.

Thorium occurs widely in nature although in small quantities. It is never found in the native state.

The important ores of thorium are given below.

Monazite sand It contains 15% of thoria along with phosphates of cerium and lanthanum. Monazite sand is found in beach sand in Travancore (India) and river sands in Brazil.

Thorite $ThSiO_4.nH_2O$. It contains 60-70% ThO_2.

Tharianite ThO_2. This mineral mainly contains uranium oxide UO_2 and ceria earths.

Extraction from monazite sand involves the following steps:

Concentration The monazite ore is concentrated by gravity separation on Wilfley tables. Further concentration is carried out by electro-magnetic separators (Monazite is magnetic and other mineral sands are non-magnetic).

Heating with conc. H_2SO_4 The concentrated ore is digested with calculated quantity of conc. H_2SO_4 at 475 K for a couple of hours in cast iron pots fitted with stirrers. Phosphates of Th, La and Ce come in the solution when cold water is added to this paste.

Addition of alkali The solution obtained above is diluted. Then alkali solution is added very carefully. Thorium phosphate gets precipitated while phosphates of La and Ce remain in solution. Thorium phosphate (with traces of phosphates of La and Ce) is filtered-off. Thorium phosphate precipitate is dissolved in H_2SO_4 and then re-precipitated.

Heating with sodium carbonate The precipitated thorium phosphate is heated with Na_2CO_3, when thorium oxide is formed. This mass is extracted with water and filtered. The residue contains thorium oxide with a little of lanthanum and cerium oxides.

Reaction with dil. H_2SO_4 The above residue is treated with dil. H_2SO_4 when solution containing sulphates of Th, La and Ce is obtained.

Addition of oxalic acid Oxalic acid is added to the above solution when oxalates of Th, La and Ce are precipitated and removed by filtration.

Treatment with ammonium oxalate The precipitate of oxalate Th, La and Ce is treated with ammonium oxalate solution. Thorium oxalate is soluble in ammonium oxalate while oxalates of La and Ce are insoluble and are removed by filtration.

Heating of ammonium thorium oxalate The filtrate containing ammonium thorium oxalate complex is heated when crude thorium oxide is obtained.

Purification of crude thorium oxide It is dissolved in nitric acid when thorium nitrate is formed which crystallizes out.

On heating thorium nitrate crystals, pure thorium oxide is obtained.

From Thorite The powdered ore is digested and evaporated with HCl. The residue is then treated with dilute HCl, tin, lead, etc. are separated by passing H_2S. The filtrate is treated with ammonia and the precipitate is dissolved in dilute H_2SO_4. On concentrating the solution, sparingly soluble $Th(SO_4)_2$ separates out which on ignition yields thoria. The mother liquor still contains some thorium and may be made available by neutralizing with K_2CO_3 and mixing with a boiling saturated solution of K_2SO_4, when the double sulphate of K and Th separates out. It is dissolved in water and precipated as $Th(OH)_4$ by ammonia which on ignition gives thoria.

Preparation of metal from ThO_2 Thorium metal readily combines with oxygen, hydrogen, nitrogen and carbon. Therefore, its extraction is rather difficult. The following steps are involved in the extraction of thorium metal from ThO_2.

Conversion into thorium tetrachloride ThO_2 is heated with phosgene (carbonyl chloride).

$$ThO_2 + COCl_2 \longrightarrow ThCl_4 + 2CO_2$$

Reduction of $ThCl_4$ $ThCl_4$ is reduced with calcium or sodium when thorium metal is obtained.

$$ThCl_4 + 2Ca \longrightarrow Th + 2CaCl_2$$
$$ThCl_4 + Na \longrightarrow Th + 4NaCl$$

Thorium metal of highest purity can be obtained by thermal decomposition of thorium tera-iodide by the filament growth process.

Fairly pure thorium is obtained by heating ThO_2 to red heat (1675 K) with calcium and calcium chloride in a bomb tube (i.e. sealed tube).

High purity thorium required for nuclear research isobtained as follows:

Elecrolytic method To solution of nitrate is added Na_2CO_3 to precipitate thorium oxy-carbonate.

Oxy-carbonate is ignited to give oxide.

ThO_2 is mixed with finely divided carbon black and reacted with chlorine at 675 K to give $ThCl_4$.

$ThCl_4$ (70 parts) and NaCl (30 parts) is electrolysed in a cell with graphite lining.

Ion-exchange method Thorium is freed from uranium by employing Amberite IR resin. Thorium so obtained is suitable for use as a breading element for atomic piles.

It is a dark grey powder.

It is hard and ductile.

Its m.p. is 2118 K, b.p. 3773 K and specific gravity 11.33.

It exhibits two allotropic forms—amorphous and crystalline.

Action of air Powdered thorium burns in air brilliantly forming oxide.

$$Th+O_2 \longrightarrow ThO_2$$

Action of hydrogen When heated, it reacts with hydrogen vigorously, thereby forming hydride.

$$Th+2H_2 \longrightarrow ThH_4$$

Action of non-metals It reacts with non-metals to form corresponding compounds.

$$Th+2X_2 \longrightarrow ThX_4 \quad \text{(halogens)}$$
$$3Th+2N_2 \longrightarrow Th_3N_4$$
$$Th+2S \longrightarrow ThS_2$$

Action of acids It is hardly attacked by dilute acids but readily dissolves in aqua regia and fuming hydrochloric acid.

Thorium finds use in the following directions.

Incandescent gas mantles (gas mantles consist of 99% of thoria and 1% ceria).

${}^{232}_{90}Th$ is fissionable when bombarded by slow neutrons. It is employed to get atomic energy by direct fission.

$${}^{233}_{90}Th+{}^{1}_{0}n \longrightarrow {}^{233}_{90}Th$$

or indirectly by changing into fissionable ${}^{233}U$

$${}^{233}_{90}Th \longrightarrow {}^{233}_{91}Pa+{}^{0}_{-1}e \xrightarrow{27\ days} {}^{233}_{92}U+{}^{0}_{-1}e$$

X-rays targets Thorium is used as strong source of monochromatic X-rays for research work.

Photo-electric cells Tungsten filament is coated (one atom thick) with thorium to increase electron emission power of the filament.

As getter in vacuum tubes 'Gettering' is a chemical cleaning process to remove residual gases from vacuum tubes.

As additive 'in alloys' Thorium is added to form alloys used for making heating elements of sun lamps, for generating ultraviolet rays.

Catalysis Thoria, because of its high melting point and sintering temperature, is a very good foundation for several catalysts employed at high temperatures.

Analytical chemistry $Th(NO_3)_4$ is used for titration of fluorides employing methyl red indicator.

$Th(NO_3)_4$ is also used for the determination of chloride, sulphate, rare earths, heavy metals and in the estimation of iron and titanium.

Thulium [Greek *Thoule*, Thyle, the northernmost region of the world] **Tm**. A Group IIIA element of the 6th period of the Periodic Table of Elements, atomic number 69, atomic mass 168 934, a lanthanide, one stable isotope, ^{169}Tm. Discovered in 1879 by Cleve.

Properties Typical for lanthanides.

Occurrence As admixture to some minerals, e.g. monazite.

Uses Mostly the radioactive isotope, ^{170}Tm, is used (radiography, medicine; its application for radiodiagnosis offers much promise for ^{170}Tm sources which are portable and do not require any special equipment and can successfully be used in place of expensive and cumbersome X-ray units).

Tin [Anglo-Saxon origin] **Sn**. A Group IVA element of the 5th period of the Periodic Table of Elements, atomic number 50, atomic mass 118.69, known to the ancients.

Properties A silvery white bright metal; ductile, slowly tarnishes in the air because of the formation of a tin oxide film; changes to the brittle grey form at temperatures below

287.2 K, which may cause the destruction of things made of tin. The oxidation states in compounds are +4 (the stablest state) and +2. Rather unreactive under usual conditions, slowly dissolves in dilute acids and alkalis.
concentrated alkalis.

Titanium [Greek *Titan*, a giant deity] **Ti.** A 3 d element of the 4th period of the Periodic Table of Elements, atomic number 22, atomic mass 47.90. Discovered by Gregor in 1789; pure metal was only prepared in 1925.

Properties A high-melting white metal, the oxidation states in compounds are +4, +3, less frequently +2; titanium dihalides are unstable substances. The reactivity of titanium increases with temperature. Highly resistant to corrosion because of the formation of a strong oxide film. Hydrochloric acid, especially hot acid, reacts with titanium; the metal is easily attacked by hydrofluoric acid.

Occurrence Rutile, TiO_2; ilmenite, $FeTiO_3$; some other minerals.

Production By reducing titanium oxide with calcium metal or calcium hydride; by reducing titanic chloride with molten sodium or magnesium metal.

Uses Mostly as alloys with aluminium, molybdenum, vanadium, manganese, and other metals. A promising structural material for aircraft, chemical equipment, and shipbuilding. The advantage of titanium alloys is their high refractoriness compared with aluminium and magnesium alloys which is important for modern aviation.

Titanium(IV) chloride. **$TiCl_4$**. It is a colourless, diamagnetic fuming liquid. Since large amount of energy is required to remove four electrons from titanium atom, therefore, all the tetrahalides, i.e. $TiCl_4$, $TiBr_4$ and TiI_4 are covalent. $TiCl_4$ is hydrolysed rapidly by water to give Ti(IV) oxide.

$$TiCl_4 + H_2O \xrightarrow{\text{partial}} TiOCl_2 + 2HCl$$

$$TiCl_4 + 2H_2O \xrightarrow{\text{complete}} TiO_2 + 4HCl$$

$TiCl_4$ finds extensive use as a catalyst in the manufacture of polyethylene. $TiCl_4$ reacts with alcohols to form alkoxides.

$$TiCl_4+4ROH+4NH_3 \dashrightarrow Ti(OR)_4+4NH_4Cl$$

Titanium(IV) oxide, TiO_2 It is a stable, non-volatile amphotertic substance. It dissolves in alkalis forming titanates.

$$TiO_2+2NaOH \longrightarrow Na_2TiO_3+H_2O$$

It also dissolves in strong acids to form species such as $[Ti(OH)_3]^+$ and $[Ti(OH)_2]^{2+}$. TiO_2 is used as white pigment in paints. TiO_2 has a rutile structure, i.e. in it each titanium atom is surrounded octahedrally by six oxygen atoms and each oxygen atom is in turn surrounded by three titanium atoms disposed towards the corners of an equilateral triangle.

Titration. In volumetric analysis, two solutions are always made to react in a conical flask known as the titration flask. One of these solutions is taken in a burette and the other in the titration flask. The solution from the burette is added to the flask. This process of finding the volume of titrant (standard solution) required to react completely with a known volume of the solution under analysis is called titration.

Tracers. A method of tracing the course of a reaction is by introducing radioactive isotopes of an element which are chemically identical. Such radioisotopes are called tracers. The course of reaction is traced or denoted by following the path of the activity accompanying the radioisotopes using suitable means, e.g. Geiger counter.

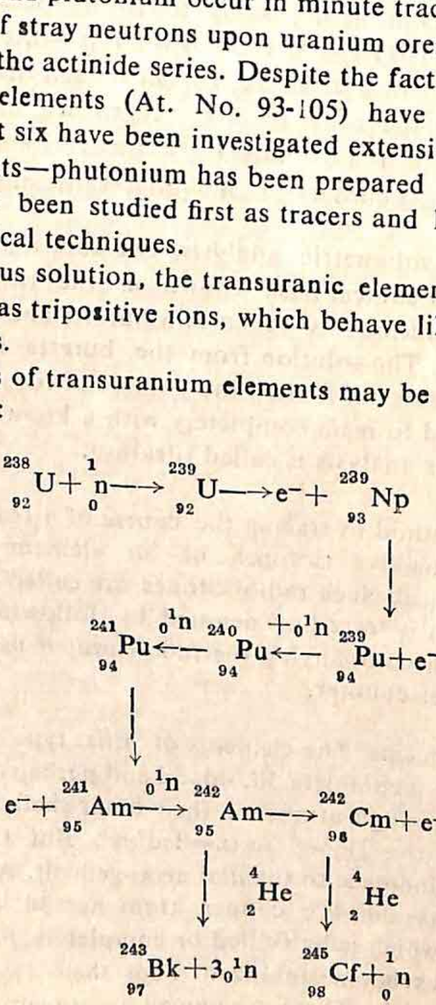
Transition elements. The elements of this type are characterized with their incomplete 3d, 4d, 5d and perhaps 6d orbitals. The electronic configurations of their outer shell are given by general structure $(n-1)d^1ns^2$ to $(n-1)d^9ns^2$. But they do not show a rigid adherence to the n^1s^2 arrangement. A Cr atom in its ground state has $3d^5\ 4s^1$; copper atom has $3d^{10}4s^1$. This is because a shell which is half-filled or completely filled is particularly strongly exchange-stabilized. Thus their two outermost shells are incomplete. These are named as transition elements.

In the periodic table these elements begin with IIIB through Group IB occupy the positions between electropositive elements of Groups IA and IIA and electronegative elements of Groups IIIA-VIIA.

Transuranic elements. Elements with atomic number higher than uranium are known as transuranic elements. These are mostly synthetic elements and do not occur in nature. Only neptunium and plutonium occur in minute traces resulting from the action of stray neutrons upon uranium ores. They constitute a part of the actinide series. Despite the fact that the thirteen transuranic elements (At. No. 93-105) have been discovered and the first six have been investigated extensively, only one of these elements—phutonium has been prepared in quantity. The others have been studied first as tracers and later on by ultra-micro chemical techniques.

In aqueous solution, the transuranic elements exist almost exclusively as tripositive ions, which behave like other positive actinide ions.

Synthesis of transuranium elements may be summarised as given below:



$$^{238}_{92}U + {}^{1}_{0}n \longrightarrow {}^{239}_{92}U \longrightarrow e^- + {}^{239}_{93}Np$$

$$\downarrow$$

$$^{241}_{94}Pu \xleftarrow{{}_0{}^1n} {}^{240}_{94}Pu \xleftarrow{+{}_0{}^1n} {}^{239}_{94}Pu + e^-$$

$$\downarrow$$

$$e^- + {}^{241}_{95}Am \xrightarrow{{}_0{}^1n} {}^{242}_{95}Am \longrightarrow {}^{242}_{96}Cm + e^-$$

$$^{241}_{95}Am \xrightarrow{{}^{4}_{2}He} {}^{243}_{97}Bk + 3{}_0{}^1n \qquad {}^{242}_{96}Cm \xrightarrow{{}^{4}_{2}He} {}^{245}_{98}Cf + {}^{1}_{0}n$$

Triple superphosphate. It is an excellent phosphatic fertilizer and is being manufactured by adding phosphoric acid to calcium phosphate.

$$Ca_3(PO_4)_2 + 4H_3PO_4 \rightarrow \underset{\text{Triple superphosphate}}{3CaH_4(PO_4)_2}$$

In order to manufacture triple superphosphate a weighed quantity of rock phosphate is reacted with 54% phosphoric acid in a mixer. The reaction product is allowed to move over a belt conveyor where it sets to a solid mass of triple superphosphate.

Triple superphosphate contains 45% available phosphorus as P_2O_5 which is about three times more concentrated than superphosphate.

In recent years the manufacture of concentrated or triple superphosphate has been increasing at a very fast rate because of high analysis. It contains 45 per cent P_2O_5. Here besides high analysis, the gypsum content is less.

Its behaviour is very similar to superphosphate. Its storage cost per unit of plant food is less due to its high analysis.

Tritium. A radioactive isotope of hydrogen with the mass number equal to 3; its nucleus consists of one proton and two neutrons (symbol T or ^3H). Half-life ($t_{\frac{1}{2}}$) 12 years, decays with the emission of beta particles. Small amounts of tritium are formed in nuclear processes. Manufactured by bombardment of lithium with slow neutrons. Tritium oxide is made by the oxidation of tritium in electric discharge. Because of the difference in masses reactions involving tritium differ in their rates from those of ordinary hydrogen. Tritium is used as a thermonuclear fuel in hydrogen bombs and energy devices. It is also used as a tracer in chemical, biological, etc. studies, to determine the origin of rains, the age of a wine or a meteorite, etc.

Triton. The nucleus of tritium, symbol ^3H, contains one proton and two neutrons, mass 3.01646. Used as a bombarding particle in cyclotrons.

Tungsten [Swiss *tung*, heavy+*sten*, stone, also called wolfram] W. A 4 d element of the 6th period of the Periodic Table of Elements, atomic number 74, atomic mass 183.85. Discovered by Scheele in 1781, first isolated by Spaniards d' Elhujar brothers.

Properties A white-grey metal, m.p. 3683 K, chemically stable under usual conditions. At elevated temperatures reacts with oxygen, carbon, and other elements, Reacts with fluorine at 295 K, with other halogens at higher temperatures. Unattacked by acids except for hydrofluoric and nitric acids. The oxidation states in compounds are +4, +5, and, most often, +6.

Occurrence In the minerals wolframite, (Fe, Mn)WO_4, and scheelite, $CaWO_4$; as admixture to tin, molybdenum and titanium ores.

Uses Alloying of steel, the manufacture of hard alloys, filaments of incandescent lamps, heating elements in electric furnaces, electrodes for welding, cathodes for vacuum-tube oscillators, high-zoltage rectifiers, etc.

Turbidimetry. The determination of the concentration of a substance from the absorption of light by suspended particles.

U

Uranium [after Uranus, the planet] **U**. An f block element of the 7th period of the Periodic Table of Elements, a radioactive element of the actinide series, atomic number 92, atomic mass 238.03. Natural uranium contains three istopes, ^{238}U (99 per cent) ^{235}U and ^{234}U. None of them is stable. The ^{238}U and ^{235}U isotopes are parent isotopes of two natural radioactive series; the final products of their decay are helium and the stable ^{206}Pb and ^{207}Pb isotopes, respectively. The accumulation of the lead isotopes in specimens containing uranium (rocks, minerals meteorites, etc.) can be used to determine the age of geological or cosmic objects. Discovered by Klaproth in 1789.

Properties A silvery chemically active metal, the oxidation states in compounds are +6 and +4. Slowly undergoes oxidation in the air to form the oxides UO_2, U_3O_8 and UO_3. Gives alloys with a number of metals.

Occurrence The chief ore is pitchblende, U_3O_8; found in natural waters, in soil.

Manufacture By the reduction of UF_4 with calcium or magnesium metals at elevated temperatures.

Uses A fissionable material (fission is induced by the capture of neutrons) used as nuclear fuel and atomic bomb explosive. Uranium salts are used in photography, in glass manufacture, and in the analytical chemistry.

Uranyl, UO_2^{2+}. A positive doubly charged U(VI) ion, plays the part of a metal ion in a number of uranium compounds, e.g. uranyl nitrate, $UO_2(NO_3)_2$. Most uranium salts are green-yellow substances soluble in water.

Urea. It is an excellent nitrogenous fertilizer and is manufactured by reacting ammonia and carbon dioxide under 200 atmosphere pressure. Ammonium carbamate is formed as an intermediate product which changes into urea under conditions of the reaction.

$$CO_2+2NH_3 \rightarrow \underset{\text{Ammonium carbamate}}{NH_2COONH_4}$$

$$NH_2COONH_4 \rightarrow \underset{\text{Urea}}{NH_2CONH_2}+H_2O$$

Urea produced separates as dry powder and contains about 47 per cent of nitrogen.

V

Valence-bond theory (VBT). The valence-bond method, developed largely by Linus Pauling, allows prediction of the geometries of coordination spheres. The central metal ion, acting as Lewis acid, accepts lone pairs of electrons from ligands into vacant metal ion orbitals.

The stepwise process of formation of a complex may thus be considered as:

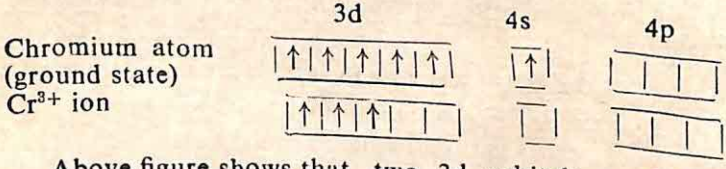
The loss of electrons by the metal in accordance with its oxidation number.

The hybridization of an appropriate number of metal orbitals for the formation of covalent bonds with the ligand orbitals. This will define the stereochemistry of the complex.

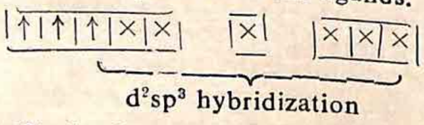
The occupation of the hybrid orbitals by the lone pairs of electrons from the ligands to form α-bonds.

This can be illustrated by applying the VB approach to an octahedral chromium(III) complex $[Cr(NH_3)_6]^+$ as under:

Chromium(III) has an outer electronic configuration $3d^3 4s^\circ$, which may be represented at:



Above figure shows that two 3d orbitals, one 4s orbital and three 4d orbitals are available to from six hybrid orbitals which can accept six electron pairs from the ligands.



Cr in $[Cr(NH_3)_6]^{3+}$ (each of the 6 NH_3 ligands donates a pair of electrons to Cr).

The complex $[Cr(NH_3)_6]^{3+}$ involves d^2sp^3 hybridization, and its structure is octachedral.

Valence Shell Electron Pair Repulsion Theory (VSEPR). This theory was put forward by R.J. Gillespie and R.S. Nyholm in the year 1963. This theory is based on the fact that the electronic cloud of one atom exerts a force of repulsion on the electronic cloud of another atom when brought close to each other. Likewise the electron belonging to one particular orbital will also exert a repulsive force on the electrons belonging to the other orbitals, i.e. the orbitals containing electrons experience a repulsion. As a result of the repulsion exerted by the electrons present in one orbital on the electrons present in the other orbitals, the orbitals tend to arrange themselves as far apart from each other as possible so that the repulsion is minimum.

It has been found that the bond pair repulsion is much less than the bond pair lone-pair repulsion which in turn is less than the lone pair-lone pair repulsion.

Vanadium. Vanadium is a silvery-white metallic transition element. It is placed in Group VB along with niobium and tantalum. Niobium and tantalum show greater resemblance to each other than to vanadium. The elements of Group VB have five valence electrons in (*n*-1)d and *n*s orbitals.

In 1867, Roscoe isolated its relationship with the nitrogen family of elements.

Vanadium does not occur free in nature. However, it occurs in many rocks. About 60 minerals having it are are known. The main ores of vanadium are as follows:

Carnotite, $K(UO_2)VO_4.nH_2O$; Patronite, $V_2S_5,3CuS_2$; Vanadinite $Pb_5(VO_4)_3Cl$ or $2Pb_3PbCl_2(VO_4)_2$. Ashes of Peruvian coal contain up to 48 per cent of vanadic oxide.

From Vanadinite After powdering the mineral it is heated with concentrated hydrochloric acid when lead is precipitated out on cooling as lead chloride, while vanadium goes into solulion in the form of complex having the formula $[V(OH)_4]Cl$. After removing lead chloride, the solution is treated with ammonia and ammonium chloride when an orange coloured precipitate of ammonium vanadate, NH_4VO_3 is obtained. This precipitate on heating yields more or less impure vanadium pentoxide.

$$Pb_5(VO_4)Cl+12HCl\rightarrow 5PbCl_2+3V(OH)_4Cl$$
$$V(OH)_4Cl+NH_4Cl\rightarrow NH_4VO_3+2HCl+H_2O$$
$$HCl+NH_3\rightarrow NH_4Cl$$
$$NH_4VO_3\rightarrow V_2O_5+2NH_3+H_2O$$

From Carnotite After fusing the ore with a mixture of sodiam carbonate and sodium nitrate, it is extracted with water when iron is removed as iron(III) hydroxide. The solution is concentrated to yield the crystals of $Na_4VO_2(CO_3)_2$. thereby leaving sodium vanadate Na_3VO_4 in the mother liquor.

Now ammonium chloride and ammonia are added to the mother liquor to get crystals of ammonium vanadate, which on fusion gives the pentoxide.

$$4K(UO_2)(VO_4)+12Na_2CO_3\rightarrow 3Na_4(UO_2)(CO_3)_3+ K_4(UO_2)(CO_3)_3+4Na_3VO_4$$
$$Na_3VO_4+3NH_4Cl\rightarrow (NH_4)_3VO_4+3NaCl$$
$$(NH_4)_3VO_4\rightarrow NH_3VO_3+2NH_3+H_2O$$
$$2NH_4VO_3\rightarrow V_2O_5+2NH_3+H_2O$$

Although the pure metal is difficult to obtain even on a small scale because of the high temperature requird and the tendency for re-oxidation, it has been obtained by the following different methods:

Vanadium is obtained by the reduction of its pentoxide with the thermite method, using mischmetal (an alloy of certain rare earth metals like Ce. La, Nd, Pr, etc. obtaiaed from the residues left after the extraction of thorium) in place of aluminium.

Vanadium is also obtained by the reduction of V_2O_5 with calcium and some calcium (as a flux) in a steel bomb at 975—1025 K.

$$V_2O_5+5Cu\rightarrow 5CaO+2V$$

Vanadium may also be obtained by the reduction of the trichloride, VCl_3 with sodium in an iron bomb or with hydrogen in a platinum boat at 975 K.

$$VCl_3+3Na \rightarrow V+3NaCl$$
$$2VCl_3+3H_2 \rightarrow 2V+6HCl$$

Vanadium may also be obtained by the reduction of the telrochloride with magnesium.

$$VCl_4+2Mg \rightarrow V+2MgCl_2$$

It is a silvery white metallic transition element; atomic number 23; m.p. 2163 K; b.p. 3653 K.

It is a hard but light metal.

It is a good conductor of electricity but allows the current to flow in one direction.

It is paramagnetic.

It is unreactive at room temperature. However, it combines with other elements readily on heating, e.g. on heating in air it gets oxidized to pentoxide, in chlorine to VCl_4 whereas with nitrogen it forms VN.

$$4V+5O_2 \rightarrow 2V_2O_5$$
$$V+2Cl_2 \rightarrow VCl_4$$
$$2V+N_2 \rightarrow 2VN$$

With carbon it forms a stable carbide.

$$4V+3C \rightarrow V_4C_3$$

Vanadium also undergoes combination with hydrogen, phosphorus, arsenic, sillicon and bromine.

It is not dissolved in cold mineral acids but dissloves in perchloric acid and in ammonium phosphates to form metavanadic acid, HVO_3. It gets dissolved slowly in hot conc. sulphuric acid, hot hydrochloric acid and hot dilute nitric acid. In these solutions; the pervanadyl ion, VO_2^+ is present.

It is dissolved in hot fused alkalis to form corresponding vanadates with the liberation of hydrogen.

$$2V+6NaOH+2H_2O \rightarrow 2Na_3VO_4+5H_2$$

It is not affected by steam.

It forms a range of complexes with oxidation states from +2 to +5.

Vanadium (90 per cent) is mainly used is making ferrovanadium which finds use in the manufacture of alloy steel.

Vanadium compounds find use in the manufacture of ink, photographic chemicals. medicines, insecticides.

Vanadium pentoxide finds use as a catalyst in the oxidation of naphthalene.

$VOCl_3$ is used as a catalyst in making ethylene-propylene rubber.

Van Arkel method. It is the method for getting ultra pure metals. Metals like hafnium, zirconium, titanium, etc. are purified by this method. It involves the conversion of a meal into its volatile unstable compound which on thermal decomposition yields pure metal. The impurities are not affected during compound formation.

Example

$$\underset{\text{(impure)}}{Ti}+2I_2 \xrightarrow{500\text{ K}} TiI_4\text{ (g)}$$

$$TiI_4 \xrightarrow{1900\text{ K}} \underset{\text{(pure)}}{Ti}+2I_2$$

Van der Waals forces. The real gases do not obey the perfect gas laws due to the existence of small cohesive forces between the gas molecules. These forces are called van der Waals forces; they arise from the attraction between induced dipoles on natural atoms or molecules, i.e. it is an indnced dipole-induced dipole bond.

Van der Waals radius. It is the distance in an atom from the nucleus to a point where electron density is negligible. It may also be regarded as a distance of closest approach within which non-bonded atoms will not interfere with one another. Alternatively it may be egarded as one-half of the distance between the centres of the nuclei of two non-bonded adjacent like atoms belonging to two neighbouring molecules in the solid state. The name is derived from van der Waals forces which are in existance between neutral atoms of noble gases and between non-polar molecules of various substonces. The van der Waals radius of any atom is greater than its covalent atomic radius.

W

Water pollution. Life is impossible without water. Good quality water is needed for drinking and innumerable other purposes. The industries discharge their effluents into water bodies leading to the general contamination of water with toxic compounds. Due to inadequate sewage disposal system, refuse gets mixed up with the water resources causing water pollution. Water pollutants originating from residential areas are mainly organic matter, excess phosphates, nitrogen compounds and suspended solids. The industrial effluents consist of heavy metals, oils, phenols, acids, etc. Most of the industries allow their waste to mix with water bodies without any treatment. As a result, these pollutants progressively collect in natural water systems, first in the surfare water and then in the ground water. Thus, water obtained for drinking or irrigation from these sources becomes polluted and causes health hazards.

Chemical pollutants harm water in several ways. Some organic pollutants act as toxins and carcinogens while others increase biological oxygen demand (BOD) of water. The BOD is a measure of the amount of dissolved oxygen consumed in the biological processes associated with the degradation of organic compounds in water. In general, the higher the BOD the more polluted a water sample is. The more oxygen consumed by micro-organisms in degrading organic compounds, the less oxygen becomes available to support the aquatic flora and fauna. Still other organic pollutants may contribute towards objectionable odour and taste of drinking water.

Werner's coordination theory. The salient features of Werner's coordination theory are:

Every element exhibits two types of valences, viz. primary valence and secondary valence.

The primary valence of the central metal ion is satisfied by negative ions. Its attachment to the metal ion is shown by dotted lines. In modern terminology it corresponds to the oxidation state of the metal atom or ion and is ionizable.

The secondary valence is satisfied by either negative ions or neutral molecules. Its attachment to the metal is shown by thick lines. It corresponds to the coordination number of the metal atom or ion and is mon-ionizable.

Every metal tends to satisfy both its primary and secondary valences. In order to meet this requirement, a negative ion may perform a dual function of satisfying both types of valences.

Every metal has a fixed number of secondary valences.

The ligands which satisfy the secondary valences are always directed towards fixed positions in space. The geometry of a complex is determined by the number and arrangement of such ligands in space. If a metal ion has a secondary valence of four, the geometry of the complex can be tetrahedral or square planar. On the other hand, if its secondary valence is six, the complex should be octahedral. The primary valences are non-directional.

In modern formulation, the complex ion is shown in square brackets with ionizable ligands outside the coordination sphere. Thus, for complexes $CoCl_3.6NH_3$, $CoCl_3.5NH_3$, $CoCl_3.4NH_3$, $CoCl_3.3NH_3$, the modern formulae can be written as under:

Werner formula	*Modern formula*	*Cation*	*Anion*	*Total number of ions*
$CoCl_3.6NH_3$	$[Co(NH_6)_6]Cl_3$	$[Co)NH_3)_6]^{3+}$	$3Cl^-$	4
$CoCl_3.5NH_3$	$[Co(NH_3)_5Cl]Cl_2$	$[Co(NH_3)_5Cl]^{2+}$	$2Cl^-$	3
$CoCl_3.4NH_3$	$[Co(NH_3)_4Cl_2]Cl$	$[Co(NH_3)_4Cl_2]^+$	Cl^-	2
$CoCl_3.3NH_3$	$[Co(NH_3)_3Cl_3]$	(non-ionizable)	—	—

White lead. White lead also known as basic lead carbonate, $Pb(OH)_2\ 2PbCO_3$ is manufactured by the action of air, carbon dioxide and acetic acid on lead.

$$2Pb+O_2\ (air)+2H_2 \longrightarrow 2Pb(OH)_2$$

$$2Pb(OH)_2+2CH_3COOH \longrightarrow \underset{\text{Basic lead acetate}}{Pb(OH)_2.Pb(CH_2COO)_2} +2H_2$$

$$Pb(OH)_2.Pb(CH_3COO)_2+Pb(OH)_2+2CO_2 \longrightarrow \underset{\text{White lead}}{Pb(OH)_2.2PbCO_3}+2CH_3COOH$$

Mixed with linsed oil, white lead is used as a white paint. It has a good covering power.

X

Xenon. A colourless, odourless, monatomic element of the nroble gas group, now known to form compounds. It occurs in trace amounts in air. Xenon is used in electron tubes and strobe lighting.

Sympol Xe; m.p. 161K; b.p. 166 K; density 5.89 kg m^{-3},

Xenon difluoride. XeF_2. In 1962 Weaks, Chermick and Matheson obtained xenon difluoride, XeF_2 by mixing xenon and fluorine in a nickel vessel and exposing the mixture to light from a high pressure mercury arc; the product so produced is rapidly cooled.

$$Xe+F_2 \xrightarrow{\text{Hg vapour}} XeF_2$$

$$\underset{\text{(ratio 1 : 3)}}{Xe+F_2} \xrightarrow[\text{670 K, 2 h}]{\text{Ni}} XeF_2$$

It is colourless crystalline solid which melts at 413 K.

It is soluble in liquid hydrogen fluoride and acts as a good fluorinating agent.

It oxidizes water, hydrogen and iodine.

$$2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$$
$$XeF_2 + H_2 \longrightarrow Xe + 2HF$$

Xenon hexafluoride, XeF_6. In 1963 Dudley, Gard and Cady obtained XeF_6 by heating xenon with a large excess of fluorine at 575 K.

$$Xe + 3F_2 \xrightarrow{Ni} XeF_6$$
$$\text{(ratio 1 : 20) 575 K, 50 atm}$$

It is a colourless crystalline solid which turns yellow at 316 K and melts at 321 K to give a yellow solid.

It is most volatile of all xenon fluorides and its vapours are yellow,

It is soluble in liquid hydrogen fluoride which is good conductor of electricity due to the formation of ions.

$$XeF_6 + HF \longrightarrow XeF_5^+ + HF_2^-$$

Xenon oxydifluoride, $XeOF_2$. It is not a very stable compound. It is prepared by slow and partial hydrolysis of XeF_4 at low temperature.

$$XeF_4 + H_2O \longrightarrow XeOF_2 + 2HF$$

There are 12 valence electrons (8 from xenon, 2 from the two fluorine atoms and 2 from oxygen atom) to be filled in orbitals, hence six orbitals are required. Therefore, two electrons from 5p orbitals shift to the 5d orbitals in excited state and hybridization around xenon is sp^3d. Now two orbitals contain lone pairs and three orbitals contain bond pairs. These three hybrid orbitals which are singly filled are used in forming bonds with one oxygen atom and two fluorine atoms. One 5d orbital which is not involved in hybridization is used in forming π bond with the oxygen atom, Thus a double bond (one σ bond and one π bond) is formed between xenon and oxygen. Although the shape of the molecule under sp^3d hybridization should be trigonal bipyramidal, but due to presence of two lone pairs of electrons, there is distortion in the structure. Hence it has T-shaped structure.

Xenon oxytetrafluoride, $XeOF_4$. In 1963 Smith obtained it by mixing xenon hexafluoride with an equimoleculer quantity of water.

$$XeF_6+H_2 \longrightarrow XeOF_4+2HF$$

It can also be prepared by the reaction of xenon fluoride with silica.

$$2XeF_6+SiO_2 \longrightarrow 2XeOF_4+SiF_4$$

Xenon tetrafluoride. XeF_4. In 1962 Classen, Selig and Malm obtained xenon tetrafluoride, XeF_4 by heating five volumes of fluorine with one volume of xenon to 670 K in a nickel can followed by rapid cooling in cold water.

$$\underset{\text{(ratio 1 : 5)}}{Xe+2F_2} \xrightarrow[\text{670 K, 5-6 atm}]{Ni} XeF_4$$

It is also a colourless crystalline solid which has a melting point of 387 K. It sublimes readily.

It is soluble in liquid hydrogen fluoride and acts as a good fluorinating agent.

$$XeF_4+2H_2 \longrightarrow Xe+4HF$$
$$XeF_4+2SF_4 \longrightarrow Xe+2SF_6$$
$$XeF_4+4HCl \longrightarrow Xe+4HF+2Cl_2$$
$$XeF_4+C_6H_6 \longrightarrow 3Xe+4BF_3+6Cl_6$$

It oxidizes iodide into iodine.

$$XeF_4+4I^- \longrightarrow Xe+4F^-+2I_2$$

It disproportionates into water and forms highly explosive solid compound, XeO_3.

$$2XeF_4+3H_2O \longrightarrow Xe+XeO_3+6HF+F_2$$

It forms addition compounds like XeF_2 does.

There are 12 valence electrons (8 from valence shell of xenon and 4 from four fluorine atoms) to be filled in orbitals, hence six orbitals are required. Therefore, xenon exhibits sp^3d^2 hybridization which gives the molecule an octahedral structure. But the two lone pairs are one above and one below the plane containing xenon and four fluorine atoms at in the same plane alongwith xenon atom. Therefore, the structure of XeF_4 is square planar.

Xenon tetroxide, XeO_4. It can be formed by the reaction of barium perxenate with anhydrous sulphuric acid.

$$Ba_2XeO_6 + 2H_2SO_4 \longrightarrow XeO_4 + 2BaSO_4 + 2H_2O$$

It is not a stable compound as the xenon trioxide. It decomposes to xenon and oxygen.

$$XeO_4 \longrightarrow Xe + 2O_2$$

X-radiation. It is an energetic form of electromagnetic radiation. The wavelength range is 10^{-11} m to 10^{-8} m. X-rays are normally produced by absorbing high energy electrons in matter. The radiation can pass through matter to some extent (hence its use in medicine and industry for investigating internal structures). It can be detected with photographic emulsions and devices like the Geiger-Muller tube.

X-ray photons result from electronic transitions between the inner energy levels of atoms. When high-enery electrons are absorbed by matter, an X-ray line spectrum results. The structure depends on the substance and is thus used in X-ray spectroscopy. The line spectrum is always formed in conjunction with a continuous background spectrum. The minimum wavelegth λ_6 corresponds to the maximum X-ray energy, W_{max}. This is equal to the maximum energy of electrons in the beam producing the X-rays. Wavelengths in the continuous spectrum above λ_o are caused by more gradual energy loss by the electrons, in the process brown as bremsstrahlung (braking radiation).

X-ray crystallography. It is the sudy of the internal structure of crystals using the method X-ray diffration.

X-ray diffraction. It is a technique which is used to determine crystal stucture by directing X-rays at the crystals and examining the diffration patterns obtained. At certain angles of incidence a series of spots are produced on a photographic plate; these spots are caused by interaction between the X-rays and the planes of the atoms, ions, or molecules in the crystal lattice. The positions of the spots are consistent with the Bragg equation $ny = 2d \sin\theta$.

Y

Ytterbium. It is a soft malleable silvery element having two allotropes and belonging to the lanthanide series of metals. It occurs in association with other lanthanides. Ytterbium has been used to improve the mechanical properties of steel.

Symbol Yb; m.p. 1092 K; b.p. 1467 K.

Yttrium. It is a silvery metallic element belonging to the second transition series. It is found in almost every lanthanide mineral, particularly monazite. Yttrium is used in various alloys, in yttrium-aluminium garnets used in the electronics industry and as gemstones, and as a catalyst. A mixture of yttrium and europium oxides is widely used as the red phosphor on television screens,

Symbol Y; m.p, 1796 K; b.p. 3646 K.

Z

Zeolites. These are aluminosilicate minerals, which occur in nature and are also manufactured for their ion-exchange properties. They are used for water softening and for sugar refining. The zeolites have an open crystal structure and used as molccular sieves.

Zinc. Zinc is a relatively active metal. It is found in nature in the form of compounds. It is an important trace element for plants and animals and is necessary for the function of several enzymes found in human body.

The average concentration in the earth's crust is estmated at 40 mg/kg. Rocks of various kinds contain 20-200 ppm zinc and the average zinc content of coal is 33 ppm. In soil the zinc concentration varies between 10 and 300 mg/kg dry weight. In sea and fresh water the concentration of zinc is around 10 $\mu g\ L^{-1}$. Drinking water generally has the same concentration as fresh water. In general, protein rich foods, such as meat and marine organisms, oysters in particular, have high concentration of zinc (10-50 mg/kg wet weight) whereas grains, vegetables and fruits are low in zinc, usually less than 5 mg/kg. Human milk contains about 3 $mg\ L^{-1}$. The refining and preparation of food may result in a decrease of the zinc conten.t In air samples from urban areas, zinc concentration range has been reported between <0.01 to 0.84 $\mu g/m^3$; in nonurban areas upper limit is 0.20 $\mu g/m^3$.

The normal levels of zinc range from 10 to 100 mg/kg in most crops and pasture plants. Zinc was early established as essential for the growth of higher plants. Insufficient concentration of zinc is a common micro-nutrition deficiency in crops and zinc addition to soil with fertilizers is common. The toxic effect of zinc has been seen at 400 ppm, although plants vary widely in their tolerance.

The highest concentration of zinc is found in the prostate, about 100 mg/kg wet weight. High levels of zinc are also found in bone, muscle, kidney and pancreas. In kidney, zinc concentration is related to cadmium concentration in such a way that an increase in cadmium concentration is followed by an approximately equimolar increase in zinc concentration. Levels of zinc in serum and plasma are normally around 1mg L^{-1}. The concentration of zinc in whold blood is about five times higher due to a ten times higher zinc content in red blood cells. Normal humans not occupationally exposed to zinc excrete average of 0.5 mg/day in urine.

Zinc finds wide industrial applications, but its most important use is to protect and preserve iron and steel products from corrosion; this accounts for over 50 per cent of the consumption. Of late, zinc is being increasingly used for coating of sheets in automobile industry and galvanizing reinforcement rods, particularly in areas prone to atmospheric corrosion. The newly developed applications of zinc include computer and communication industries and rechargeable zinc air cells. Zinc also finds its use in agriculture as zinc sulphate which is an essential micronutrient in soils for increasing agricultural output. Other uses of zinc include alloying element in diecasting alloys, brass and in dry cells. A major application of zinc is in the form of alloys. Brasses are copper-zinc alloys containing 5 to 40 per cent of zinc. Brass tubes and sections find wide usage in heat exchangers, refrigeration equipment, electrical, commnnication equipment and electronic devices. Zinc diecastings in variety of shapes and sizes are used in motor vehicles, machinery, builders, hardware, sanitary fittings, scientific and electronic equipment. Zinc dust is used in primers and paints, for precipitation of noble metals from solutions, in the electrolytic zinc production for purification of zinc sulphate liquor, in sherardizing process to provide a protective coat to nuts, bolts and small parts. Zinc in the form of oxide and sulphide is used in substantial tonnages as pigment in paints, rubber, linoleum and similar products. Zinc chemicals are used in corrorsion inhibiting primers, welding and soldering fluxes, chemical catalysts, fungicides and pharmaceuticals. Zinc ferrrites are used in electrical devices in transformers. amplifiers, coils, motors and tuners and in electronic devices in radio, television and computers.

Zinc in ores at the concentrating mill is often determined polarographically and mill slurries are commonly monitored continuously for zinc by X-ray fluorescence to control addition of flotation reagent. Low zinc concentrations in solution are analyzed polarographically or by atomic absorption spectroscopy (AAS) with a detection limit as low as 0.01 μg/mL. The limit of detection of AAS is sufficient to permit measurements of zinc in air and in most biological materials such as tissues, blood serum and urine. X-ray analysis is also used for qualitative and semiquantitative analysis. Those methods detect zinc concentrations as low as 1 μg/mL. Polarography is still employed for water samples containing 0.01-10 mg Zn/L but is being replaced by AAS.

The committee on medical and biological effects of environmental pollutants of the National Research Council presents a well-referenced review of zinc sampling and analysis as they pertain to physiological media, water, air, foods, soils and plants. Most analysis today are by AAS which uses the 213.8 nm wavelength for zinc with reported sensitivities of 0.010-0.025 μg/mL.

Though XRF and AAS methods are very convenient from the analyst's point of view but the acccssibility of the instrumental facility to a common analyst/chemist becomes a hurdle in the choice and one looks for some alternate instrument and method. Spectrophotometric methods then become the methods of choice. Spectrophotometric procedures are popular, commonly employing dithizone (dipheylthiocarbazone) and zincon to develop red (535 nm) and blue (600 nm) colours respectively.

Zincate. It is a salt containing the ion ZnO_2^{2-}.

Zinc-blende structure. It is a from of crystal structure that consists of a zinc atom surrounded by four sulphur atoms arranged tetrahedrally; each sulphur atom is similarly surrounded by four atoms of zinc. Zinc sulphide crystallizes in the cubic system. Covalent bonds of equal strength and length result in the formation of a giant molecular structure. If the zinc and sulphur atoms are replaced by carbon atoms diamond structure is produced. Wurzite (another form of zinc sulphide)is similar but belongs to the hexagonal crystal system.

Zinc chloride, $ZnCl_2$. It is a white crystalline solid preparrd by the action of dry hydrogen chloride or chlorine on heated zinc. The anhydrous product undergoes sublimation. The hydrated salt may be prepared by the addition of excess zinc to dilute hydrochloric acid and crystallization of the solution. Hydrates with 4, 3, 5/2, 3/2 and 1 molecule of water exist. Zinc chloride is extremely deliquescent and dissolves easily in water. It is used in dentistry, Leclanche cells, as a flux, and as a dehydrating agent in organic reactions.

Zinc group. It is a group of metallic elements in the periodic table, consisting of zinc (Zn), cadmium (Cd), and mercury (Hg). The elements all occur at the end of the three transition series and all have outer $d^{10}s^2$ configuration; Zn [Ar] $3d^{10}4s^2$, Cd [Kr]$4d^{10}s^2$, Hg [Xn]$5d^{10}6s^2$' The elements all use only outer s-electrons in reactions and in combination with other elements unlike the coinage metals, which immediately precede them. Thus all form dipositive ions, and exidation states higher than +2 are not known. In addition mercury forms the mercurous ion, sometimes written as Hg(I), but actually the ion $^+Hg—Hg^+$. Although the elements fall at the end of the transition series their properties are more like those of main-group elements than of transition elements.

Zirconium. The element of titanium group—titanium, zirconium and hafrium—constitute Group IVB of the periodic table. These are d-block elements having the configuration $(n\text{-}1)\ d^2ns^2$ These are all metals with high melting and boilings points.

Zirconium does not occur free in nature but is found widely distributed. It comprises about 0.028 per cent of the earth's crust. But it is considered to be rare on account of its only a few concentrated sources. The chief sources of zirconium are:

Zircon, $ZrSiO_4$
Baddeleyite, ZrO_2
Alvite, $MSiO_4.nH_2O$ (M=Hf, Th, Zr

The sands of Travancore (India) contain fair amounts of zirconium in the form of its oxide (ZrO_2) known as zirconia.

Zirconium is extracted mainly from its ores baddeleyite and zircon.

From baddeleyite

The ore baddeleyite after it is finely pulversied is fused either with caustic soda or soda ash to convert it into sodium zirconate (Na_2ZrO_3). Fusion with soda ash requires higher temperature than the fusion with caustic soda.

$$ZrO_2+Na_2CO_3 \rightarrow NaZrO_3+CO_2$$
$$ZrO_2+2NaOH \rightarrow Na_2ZrO_3+H_2O$$

The product sodium zirconate is sintered and extraced with water. The zirconate is hydrolysed to obtain the insoluble hydrated oxide, $ZrO_2.H_2O$.

$$Na_2ZrO_3+2H_2O \rightarrow ZrO_2H_2.O\downarrow+2NaOH$$

The mass is extracted with hydrochlonic acid and the solution on evaportion yields the crystals of zirconyl chloride.

$$ZrO_2+H_2O+2HCl \rightarrow ZrOCl_2+2H_2O$$

The crystals are redissolved in water and the solution of $ZrOCl_2$, hydrated ZrO_2, is precipitated by ammonia. On ignition, it gives zirconium dioxide.

From zircon Zircon is best decomposed by fusion method. The pulverized zircon is fused with 4-6 times its mass of KHF_2.

$$ZrSiO_4+8KHF_2 \rightarrow K_2ZrF_6+K_2SiF_6+4KF+H_2O$$

The product is extracted with hot water and then filtered to separate the insoluble K_2SiF_6. The filtrate on cooling deposits the crystals of potassium fluozirconate.

Pulverised zircon is fused with caustic soda or soda ash (Na_2CO_3) so that it is converted into a mixture containing sodium zirconate and sodium silicate.

$$ZrSiO_4+4NaOH \rightarrow Na_2ZrO_3+Na_2SiO_3+2H_2O$$

Na_2ZrO_3 is converted into ZrO_2 as described in the case of baddeleyite ore.

The finely-pulverized zircon is mixed with lime and carbon. The mixture is heated to a high temperture when zirconium carbide (ZrC) is formed. The product is then extracted with water and HCl, leaving behind zirconium carbide. It is converted into $ZrCl_4$ by treatment with chlorine at 675 K.

$$ZrC + 2Cl_2 \rightarrow ZrCl_4 + C$$

Zirconium tetrachloride is then treated with NH_4OH to yield zirconium hydroxide which on ignition is converted into ZrO_3.

$$ZrCl_4 + 4NH_4OH \rightarrow Zr(OH)_4 + 4NH_4Cl$$
$$Zr(OH)_4 \rightarrow ZrO_2 + 2H_2O$$

The separation of iron and titanium from zirconium has been widely studied. This can by carried out by:

The action of sulphurous acid on neutral solution of their corresponding salts.

The hydrolysis of zirconium sulphate whereby basic sulphate hydroxide is precipitated. It is used for large-scale operation.

The action of water on an etheral solution of the respective chloride.

When sodium thiosulphate is added to a boiling solution of zirconium, salt containing free acid, zircon, thoria, and titanium are precipitated, leaving behind iron, aluminium and rare earths.

Purification of zirconium Concentrated sulphuric acid is poured into a fairly concentrated aqueous solution of zirconium sulphate or chloride whereupon a dense white crystalline precipitate of $Zr(SO_4)_2.H_2O$ is formed. The precipitate is dissolved in equal weight of water and the hydrated sulphate is precipitated several times to obtain zirconium of high purity. Best results are obtained by adding one volume of concentrated sulphuric acid to two volumes of concentrated zirconium solution a small amount of HCl is to be added during recrystallization to prevent the precipiation of any iron that may be present as an impurity.

Pure zirconium is difficult to obtain. The oxide is very stable and is not reduced by H_2. The following are the methods which produce metal in the pure form.

Reduction of fluozirconate Dry K_2ZrF_6 is mixed with potassium and then heated at a low temperature in an iron tube.

$$K_2ZrF_6 + 4K \rightarrow 6KF + Zr$$

Cold mass is washed many times with dil. HCl and a solution of NH_4Cl. It is finally washed with alcohol to get the metal zirconium.

The reduction can also be carried out with aluminium but at high temperature.

$$3K_2ZrF_6 + 4Al \rightarrow 6KF + 4AlF_3 + 3Zr$$

Reduction of halides. (*Kroll Process*). This process requires the sublimation of zirconium tetrachloride into molten magnesium metal when zirconium is obtained by displacement.

$$ZrCl_2 + 2Mg \rightarrow Zr + 2MgCl_2$$

$MgCl_2$ is removed by washing with water.

Zirconium can also be obtained by reducing $ZrCl_4$ with Na or Al in an evacuted iron tube.

$$ZrCl_4 + 4Na \rightarrow Zr + 4NaCl$$
$$3ZrCl_4 + 4Al \rightarrow 3Zr + 4AlCl_3$$

A very pure from of zirconium metal may be best obtained by dissociating the vapour of zirconium tetraiodide (ZrI_4) on tungsten metal filament at 1275-1775 K. But this method is costly one.

$$ZrI_4 \rightarrow Zr + 2I_2$$

Electrolytic reduction On electrolysing the solution of $ZrCl_4$ mixed with a small proportion of $FeCl_3$ zirconium is deposited at the cathode.

Zirconium metal (m.p. 2123 K) like titanium, is hard and corrsion resistant, resembling stainless steel in appearance. Like titanium, this metal is fairly resistant to acids and it is best dissolved in HF where the formation of anionic fluoro complexes is important in the stabilization of the solutions. Zirconium will burn in air at high temperature reacting more rapidly with nitrogen than with oxygen, to give a mixture of nitride, oxide and oxonitride, Zr_2ON_2.

Zone refining. This is used for preparing extremely pure metals. This involves the principle that when impure metal in its molten from is solidified, crystals of pure metal get deposited leaving behind impurities in the molten part of the metal. Germanium, silicon and tellurium are purified by this method.

Here, one end of a rod of the impure metal is ignited by high frequency induction furnace. It melts a narrow region at one end. Now molten region is transferred from one end of the rod to the other by moving the induction furnace slowly along the rod. The impurities collect in the molten form and pure crystals of metal separate out. For greater purification, the process is repeated for a large number of times.

APPENDIX

Distribution of Electrons in Atoms

Atomic number	*Element*	*K*	*L*	*M*	*N*
1	H	1			
2	He	2			
3	Li	2	1		
4	Be	2	2		
5	B	2	3		
6	C	2	4		
7	N	2	5		
8	O	2	6		
9	F	2	7		
10	Ne	2	8		
11	Na	2	8	1	
12	Mg	2	8	2	
13	Al	2	8	3	
14	Si	2	8	4	
15	P	2	8	5	
16	S	2	8	6	
17	Cl	2	8	7	
18	Ar	2	8	8	
19	K	2	8	8	1
20	Ca	2	8	8	2

(Contd.)

Distribution of Electrons in Atoms—*Contd.*

Atomic number	*Element*	*K*	*L*	*M*	*N*	*O*
21	Sc	2	8	9	2	
22	Ti	2	8	10	2	
23	V	2	8	11	2	
24	Cr	2	8	13	1	
25	Mn	2	8	13	2	
26	Fe	2	8	14	2	
27	Co	2	8	15	2	
28	Ni	2	8	16	2	
29	Cu	2	8	18	1	
30	Zn	2	8	18	2	
31	Ga	2	8	18	3	
32	Ge	2	8	18	4	
33	As	2	8	18	5	
34	Se	2	8	18	6	
35	Br	2	8	18	7	
36	Kr	2	8	18	8	
37	Rb	2	8	18	8	1
38	Sr	2	8	18	8	2
39	Y	2	8	18	9	2
40	Zr	2	8	18	10	2
41	Nb	2	8	18	12	1
42	Mo	2	8	18	13	1
43	Tc	2	8	18	13	2

(Contd.)

Atomic number	*Element*	*K*	*L*	*M*	*N*	*O*	*P*
44	Ru	2	8	18	15	1	
45	Rh	2	8	18	16	1	
46	Pd	2	8	18	18	0	
47	Ag	2	8	18	18	1	
48	Cd	2	8	18	18	2	
49	In	2	8	18	18	3	
50	Sn	2	8	18	18	4	
51	Sb	2	8	18	18	5	
52	Te	2	8	18	18	6	
53	I	2	8	18	18	7	
54	Xe	2	8	18	18	8	
55	Cs	2	8	18	18	8	1
56	Ba	2	8	18	18	8	2
57	La	2	8	18	18	9	2
58	Ce	2	8	18	20	8	2
59	Pr	2	8	18	21	8	2
60	Nd	2	8	18	22	8	2
61	Pm	2	2	18	23	8	2
62	Sm	2	8	18	24	8	2
63	Eu	2	8	18	25	8	2
64	Gd	2	8	18	26	9	2
65	Tb	2	8	18	27	8	2
66	Dy	2	8	18	28	8	2
67	Ho	2	8	18	29	8	2
68	Er	2	8	18	30	8	2
69	Tm	2	8	18	31	8	2
70	Yb	2	8	18	32	8	2

(*Contd.*)

Distribution of Electrons in Atoms

Atomic Number	*Element*	*K*	*L*	*M*	*N*	*O*	*P*	*Q*
71	Lu	2	8	18	32	9	2	
72	Hf	2	8	18	32	10	2	
73	Ta	2	8	18	32	11	2	
74	W	2	8	18	32	12	2	
75	Re	2	8	18	32	13	2	
76	Os	2	8	18	32	14	2	
77	Ir	2	8	18	32	15	2	
78	Pt	2	8	18	32	17	1	
79	Au	2	8	18	32	18	1	
80	Hg	2	8	18	32	18	2	
81	Tl	2	8	18	32	18	3	
82	Pb	2	8	18	32	18	4	
83	Bi	2	8	18	32	18	5	
84	Po	2	8	18	32	18	6	
85	At	2	8	18	32	18	7	
86	Rn	2	8	18	32	18	8	
87	Fr	2	8	18	32	18	8	1
88	Ra	2	8	18	32	18	8	2
89	Ac	2	8	18	32	18	9	2
90	Th	2	8	18	32	18	10	2
91	Pa	2	8	18	32	20	9	2
92	U	2	8	18	32	21	9	2
93	Np	2	8	18	32	23	8	2
94	Pu	2	8	18	32	24	8	2
95	Am	2	8	18	32	25	8	2
96	Cm	2	8	18	32	25	9	2
97	Bk	2	8	18	32	27	8	2
98	Cf	2	8	18	32	28	8	2
99	Es	2	8	18	32	29	8	2
100	Fm	2	8	18	32	30	8	2
101	Md	2	8	18	32	31	8	2
102	(No)	2	8	18	32	32	8	2
103	(Lr)	2	8	18	32	32	9	2
104	Ku	2	8	18	32	32	10	2

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